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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

O I P E
 JAN 13 2004
 P A T E N T & T R A D E M A R K O F F I C E
 A P P L I C A T I O N
 A P P E A L S
 A N D I N T E R F E R E N C E S

Applicant	:	Sven Lindfors et al.)	Group Art Unit 1765
Appl. No.	:	09/835,931)	
Filed	:	April 16, 2001)	
For	:	METHOD OF GROWING A THIN FILM ONTO A SUBSTRATE)	
Examiner	:	Kunemund, Robert M.)	

ON APPEAL TO THE BOARD OF PATENT APPEALS AND INTERFERENCESAPPLICANT'S BRIEF

Commissioner for Patents
 P.O. Box 1450
 Alexandria, VA 22313-1450

Dear Sir:

Applicant, in the above-captioned patent application, appeals the final rejection of
 Claims 1-33. This appeal is proper under 35 U.S.C. §134 and 37 C.F.R. § 191(a).

This appeal brief is filed in triplicate. A check in the amount of \$330 is included to cover
 the fee for filing the appeal brief pursuant to 37 C.F.R. § 1.17(c). Please charge any additional fees
 which may be required to Deposit Account No. 11-1410.

I. STATEMENT OF INTEREST

Pursuant to 37 C.F.R. § 1.192(c)(1), Applicant hereby notifies the Board of Patent Appeals
 and Interferences that ASM International N.V., a Netherlands corporation with its principle place
 of business at Jan van Eycklaan 10 3723 BC Bilthoven, THE NETHERLANDS, has acquired the

entire right, title and interest to the above-captioned patent application by virtue of an assignment from ASM Microchemistry OY, a Finnish corporation having offices at Kutojantie 2B, 02630 Espoo, Finland. A copy of this assignment executed on November 26, 2003 and recorded on December 17, 2003 is provided in the Appendix B. ASM Microchemistry OY obtained the entire right, title and interest to the above-captioned patent application by virtue of an assignment from the inventors. That assignment is recorded in the U.S. Patent and Trademark Office at Reel/Frame 012029/0763.

II. RELATED APPEALS AND INTERFERENCES

Pursuant to 37 C.F.R. § 1.192(c)(2), Applicant hereby notifies the Board of Patent Appeals and Interferences that Applicant, Applicant's legal representative, and ASM International N.V., are unaware of any appeals or interferences that will directly affect, or will be directly affected by, or have any bearing on the Board's decision in the pending appeal.

III. STATUS OF THE CLAIMS AND AMENDMENTS

Claims 1-33 are pending.

Claims 34-67 have been canceled in an amendment filed in a separate paper.

Claims 1-33 stand rejected under 35 U.S.C. § 103(a) upon the grounds set forth in the Final Office Action.

Claims 1-33 are the subject of this appeal.

In accordance with 37 C.F.R. § 1.192(c)(9), a copy of the claims involved in the appeal are contained in the Appendix (Appendix A) attached hereto.

IV. SUMMARY OF THE INVENTION

In the atomic layer deposition (ALD) technique, one or two or more different reactants are sequentially and/or alternatingly supplied to a reaction chamber in a pulse-wise manner. The reactants are supplied to the reaction chamber in the vapor state or in the gaseous state.

Furthermore, the reactants used in ALD are typically mutually very reactive, even at room temperature. Therefore two or more reactants or subsequent pulses of the same reactant used in ALD should be kept well separated and supplied to the reactor strictly sequentially.

Accordingly, an embodiment of the present invention relates to a method for growing thin films onto a surface of a substrate by exposing the substrate to alternately repeated surface reactions of vapor-phase reactants. The method comprises providing a first reactant source and providing an inactive gas source. A first reactant is fed from the first reactant source in the form of repeated pulses to a reaction chamber via a first conduit. The first reactant is allowed to react with the surface of the substrate in the reaction chamber. Inactive gas is fed from the inactive gas source into the first conduit via a second conduit that is connected to the first conduit at a first connection point so as to create a gas phase barrier between the repeated pulses of the first reactant entering the reaction chamber. The inactive gas is withdrawn from the first conduit via a third conduit connected to the first conduit at a second connection point.

This embodiment provides a novel method for forming a gas phase barrier between repeated pulses of the first reactant. Specifically, through switching of an inert gas flow, the reactant vapor flow is alternatingly: (i) directed to the reaction chamber by an inert gas flow from the source container towards the reaction chamber and then (ii) prevented from flowing from the source container to the reaction chamber by an inert gas flow in a reverse direction in a part of the conduit connecting the source container and the reaction chamber. For embodiments that utilize more than one reactant, this embodiment also provides a gas phase barrier between pulses of a first reactant and a second reactant. In such embodiments, strict separation of two mutually reactive reactants, as required in ALD, can be achieved in a reliable way. One advantage of these method is that the switching valves may be configured such that they are only exposed to inert gas and not

to aggressive reactants that could corrode the valves. Furthermore, the valves can be installed outside the reactor's hot zone without a risk of condensing low vapor pressure reactant.

With reference to a specific embodiment of the invention, which is described in the Specification at page 14, line 9 to page 15, line 26 and illustrated in Figure 2, a first reactant source 24 and an inactive gas source 29 are provided. Page 14, lines 14-17. A first reactant is fed from the first reactant source 34 in the form of repeated pulses to a reaction chamber 27 via a first conduit 34. Page 14, line 18 to Page 15, line 13. The first reactant is allowed to react with the surface of the substrate in the reaction chamber 27. *Id.* Inactive gas is fed from the inactive gas source 21 into the first conduit 34 via a second conduit that is connected to the first conduit at a first connection point so as to create a gas phase barrier (See Figure 2 in Appendix B) between the repeated alternating pulses of the first reactant entering the reaction chamber 27. *Id.* The inactive gas is withdrawn from said first conduit via a third conduit 33 connected to the first conduit 34 at a second connection point. *Id.*

In another embodiment, which is described in the Specification at page 11, line 23 to page 13, line 20 and illustrated in Figure 1, the first reactant pulses that are separated from one another may be alternated with similar pulses of a second reactant.

V. ISSUE PRESENTED ON APPEAL

The following issue is presented: Whether the combination of Leskela et al. (M. Leskela et. al., "Synthesis of oxide thin films and overlayers by atomic layer epitaxy for advanced applications," Materials Science and Engineering Vol. B41 (1996), pages 23-29) in view of Manasevit et al. (U.S. Patent No. 4,066,481) was properly used to reject Claims 1-33 under 35 U.S.C. § 103.

VI. GROUPING OF THE CLAIMS

For the purposes of this appeal only, all of the appealed claims stand or fall together so as to simplify and narrow the issues on appeal. While the patentability of each claim will not be discussed individually, each claim does present distinct issues of patentability and Applicant respectfully reserves the right to separately argue in future continuing applications.

Group 1: Claims 1-33

VII. DISCUSSION OF THE REFERENCES RELIED UPON BY THE EXAMINER

In rejecting the claims, the Examiner relied upon the following references:

Leskela et al.. (M. Leskela et. al., "Synthesis of oxide thin films and overlayers by atomic layer epitaxy for advanced applications," Materials Science and Engineering Vol. B41 (1996), pages 23-29) (Appendix C)

Leskela et al. provides an overview of atomic layer deposition ("ALD") chemistry. Leskela et al. is divided into five sections. In the first section (i.e., the Introduction), Leskela et al. provided an overview of the alternately pulsed reaction sequence that is common in ALD. In this sequence, "[g]aseous precursors are introduced one at a time to the substrate surface and between pulses the reactor is purged with an inert gas or evacuated. In the first reaction step, the precursor is saturatively chemisorbed at the substrate surface and during subsequent purging the excess precursor is removed from the reactor. In the second step the other precursor is introduced on the

substrate and the desired film growth takes place. After that the reaction byproducts and the precursor excess are purged out from the reactor.” Page 837. In the second section, Leskela et al. described the basic requirements of ALD precursors, which include volatility and sufficient vapor pressure. See pages 837-838. In the third section, Leskela et al. described precursor combinations and the surface as a reactant. In the fourth section, Leskela et al. described the chemistry of several non-metal and metal precursors. In the final section, Leskela et al. outlined future challenges in ALD, which included ALD precursor development.

Thus, Leskela et al. is relied upon for teaching standard ALD sequences including inert gas purges steps between reactant pulses.

Manasevit et al.(U.S. Patent No. 4,066,481) (Appendix D)

With reference to Figure 3, Manasevit et al. disclosed a reactor system 20, which may be used to epitaxially form a multilayer composite 13. Col. 3, lines 29-30. The system 20 includes a reactor chamber 21. The reactant gases enter the reactor chamber 21 via an inlet line 24. Col. 3, lines 46-46. The system 20 uses bubbler tanks 31, 32, 33 to supply reactants to the reactor chamber 21. Col. 3, lines 49-50. The carrier gas flows from a source 37 through a liquid nitrogen cold trap 38 and through an assembly 39 of valve-controlled flow meters. Col. 3, lines 59-63. The carrier gas can then be directed at a controlled rate through any or all of a series of valves 41, 42, 43, 44, respectively, (with a second series of valves 81, 82, 83 and 84 being closed) into the bubbler tanks 31, 32, 33, 34 thereby transporting the desired reactant constituents in the bubblers through a series of tank exit valves 46, 47, 48, 49. Col. 3, lines 63-68. The constituents are then transported through another series of valves 51, 52, 53, 54 and, after proper mixing, through a final valve 62 to the inlet line 24 and the reactor chamber 21. Col. 4, lines 1-5. The spent reactant gases are exhausted from the chamber 21 via an exhaust line 25 and an exhaust valve 63. *Id.*

Manasevit et al. described a method of using the system 20 as including: "1) evacuating the reactor chamber 21; 2) filling and flushing the reactor chamber with flowing hydrogen; 3) heating the pedestal 22 and pedestal-supported substrate 12 to the deposition temperature; 4) equilibrating the flow of gas from the bubbler tanks by connecting the appropriate tanks to exhaust (via valves 66, 67, 68, 69 and 72) and bubbling hydrogen therethrough at a controlled rate to equilibrate the flows at a predetermined ratio; 5) directing reactant gases into the reactor chamber to form the film of IVA-VIA compound or alloy; and 6) cooling the deposition composite to room temperature with hydrogen after diverting the reactant gases from the reactor." Col. 4, lines 8-20.

In step 4, equilibrating the flow of gas from the bubbler tanks, involves diverting the hydrogen gas through valves 51, 52, 53 and 54 to exhaust (while valves 66, 67, 68 and 69 and common vacuum valve 70 are closed) and equilibrate the flows through the exhaust valves 75, 72 at a predetermined ratio. Col. 4, lines 39-49 In step 5, reactant gases are directed to the reaction chamber, by opening valve 62 and closing the exhaust valve 75. Col. 4, lines 50-65. In this manner, the reactant gases are channeled into a single line, inlet line 24, prior to entering the reactor chamber. *Id.* By channeling the reactant gases into the single inlet line 24, the gases, which are mixed externally to the heated reactor chamber, can be introduced simultaneously into the reactor, thereby precluding an undesirable premature reaction of individual reactants with the heated substrate. *Id.* In step 6, the reactant gases are diverted from the reactor chamber 21 by closing valve 62 and opening the exhaust valve 75. *Id.*

Thus, Manasevit et al. merely discloses maintenance of a reactant flow while alternately diverting that flow through the reaction chamber and directly to exhaust.

VIII. ARGUMENT

A. The Combination Does Not Render Obvious the Method of Growing Thin Films onto a Surface of a Substrate as recited in Claims 1-33.

Claims 1-33 stand rejected under 35 U.S.C. § 103. The rejection of all of these Claims relies on the combination of Leskela et al. and Manasevit et al. However, this combination of references does not establish *prima facie* obviousness for the reasons set forth below.

Claim 1 recites method for growing thin films onto a surface of a substrate by exposing the substrate to alternately repeated surface reactions of vapor-phase reactants. The method comprises providing a first reactant source and providing an inactive gas source. A first reactant is fed from the first reactant source in the form of repeated alternating pulses to a reaction chamber via a first conduit. The first reactant is allowed to react with the surface of the substrate in the reaction chamber. Inactive gas is fed from the inactive gas source into the first conduit via a second conduit that is connected to the first conduit at a first connection point so as to create a gas phase barrier between the repeated alternating pulses of the first reactant entering the reaction chamber. The inactive gas is withdrawn from said first conduit via a third conduit connected to the first conduit at a second connection point.

The combination of Leskela et al. and Manasevit et al. does not set forth a *prima facie* case of obviousness. A *prima facie* case of obviousness requires that “all the claim limitations must be taught or suggested by the prior art.” *M.P.E.P. 2143.03*.

With respect to Leskela, this reference merely taught that in an ALD reactor “[g]aseous precursors are introduced one at a time to the substrate surface and between pulses the reactor is purged with an inert gas or evacuated.”

With respect to the Manasevit et al., this reference merely taught a reactor system that includes a reactor, a plurality of reactant sources, and a multitude of interconnected conduits and

valves for supplying the reactant to the reactor. *Importantly*, in the disclosed method for operating this reactor system, the valve 62 is opened and closed to permit or prevent the flow of the reactant to the reactor 21. *See* Col. 4, lines 50-54 and Col. 5, lines 4-8.

As such, Leskela et al. and Manasevit et al. do not teach or suggest, either alone or in combination, a method in which inactive gas is fed from the inactive gas source into the first conduit via a second conduit that is connected to the first conduit (which provides reactant) at a first connection point so as to create a gas phase barrier between the repeated alternating pulses of the first reactant entering the reaction chamber. The applied references also do not teach or suggest, either alone or in combination a method in which inactive gas is withdrawn from said first conduit via a third conduit connected to the first conduit at a second connection point. The Examiner has also not identified any suggestion in the references themselves or in the knowledge generally available to one of ordinary skill in the art to modify the references to include these operational steps. Thus, the Examiner has not set forth a *prima facie* case of obviousness.

In the Office Action dated September 11, 2002, the Examiner stated that it “would have been obvious to one of ordinary skill in the art to modify the Leskela et al reference by the teachings of the Manasevit et al reference to use the gases feed system of Manasevit et al. in order to obtain more uniform flows as set forth in the prior art.” However, as pointed out above, such a combination does not teach or suggest all of the claim limitations of Claim 1.

In response to Applicant arguments, in the final office action, the Examiner stated:

The Manasevit reference teaches the separate [and] controllable inert gas line which clearly meets the apparatus limitations of the inert gas supply line as claimed. Applicants are arguing the operational differences between the claims and the prior art. However, the instant claims are drawn to an apparatus only, and thus the prior art must merely meet the apparatus limitations and be capable of the use. In the instant case the combination of Manasevit and Leskala et al teach the claimed apparatus deposition system and due to the valves and bypasses in the references, the combined apparatus is clearly capable of being operated as shown in the specification.”

(emphasis added)

However, Claims 1-33 are method claims, which recite a number of specific operational steps as referenced above. Without admissions, Applicant submits that even if the combination had the capability to meet the claimed invention, the rejection of Claims 1-33 cannot be properly maintained by showing that the prior art “merely meet[s] the apparatus limitations and [is] capable of the use. Instead, to establish a *prima facie* case of obviousness, the Examiner must show that all of the operational steps of Claims 1-33 are taught or suggested by Leskela et al and Manasevit et al. See MPEP 2143.03. Applicants respectfully submit that the Examiner has not met this burden and cannot meet this burden by merely stating that the prior art “meets the apparatus limitations and is capable of the use.”

IX. CONCLUSION

Nothing in the prior art discloses, teaches or suggests the invention recited by the claims discussed above. In combination, the applied references also do not also art disclose, teach or suggest the invention recited by the claims discussed above. In addition, the art of fails to supply any motivation or suggestion to modify the applied references to include the limitations of the claims. The applied combinations of references therefore is improper.

The applied reference thus do not make the invention obvious. The final rejection of Claims 1-33 based on obviousness should be reversed. Favorable action to this end therefore is most respectfully solicited.

Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR

Dated: 1-6-09

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APPENDIX A

1. **(Previously presented)** A method for growing thin films onto a surface of a substrate by exposing the substrate to alternatively repeated surface reactions of vapor-phase reactants, the method comprising the steps of:

 providing a first reactant source;

 providing an inactive gas source;

 feeding a first reactant from the first reactant source in the form of repeated alternating pulses to a reaction chamber via a first conduit;

 allowing the first reactant to react with the surface of the substrate in the reaction chamber;

 feeding inactive gas from the inactive gas source into the first conduit via a second conduit that is connected to the first conduit at a first connection point so as to create a gas phase barrier between the repeated alternating pulses of the first reactant entering the reaction chamber; and

 withdrawing the inactive gas from said first conduit via a third conduit connected to the first conduit at a second connection point.

2. **(Original)** The method of Claim 1, further comprising the step of providing the second connection point upstream of the first connection point so that, at least for some length of the first conduit, the inactive gas fed into the first conduit flows upstream towards the first reactant source.

3. **(Original)** The method according to Claim 1, wherein the step of providing a first reactant source comprises vaporizing the first reactant.

4. **(Original)** The method according to Claim 3, wherein the step of providing a first reactant source further comprising maintaining the first reactant source at least at a vaporizing temperature of the first reactant.

5. **(Original)** The method of Claim 1, wherein the step of providing a first reactant source comprises freeing solid reactant from solid particles located within the first reactant source.

6. **(Original)** The method of Claim 1, wherein the step of providing a first reactant source comprises freeing liquid reactant from a suspended liquid in the first reactant source.

7. **(Original)** The method of Claim 1, further comprising the steps of providing a purifier and passing the first reactant through the purifier before transferring the first reactant into the reaction chamber.

8. **(Original)** The method of Claim 7, wherein the purifier is a filter comprising at least one of a ceramic molecular sieve and an electrostatic filter capable of separating one of at least dispersed liquid, solid droplets, particles and molecules of a minimum molecular size from the reactant gas flow.

9. **(Original)** The method according to Claim 7, wherein the purifier is an active purifier comprising functional groups capable of reacting with components present in the reactant gas flow.

10. **(Original)** The method of Claim 7, wherein the step of providing a purifier further includes providing the purifier along the first conduit between the second connection point and the first reactant source.

11. **(Original)** The method of Claim 10, further including only passing the first reactant over the purifier in a signal direction.

12. **(Original)** The method according to Claims 10, further comprising the step of forming the gas phase barrier between the purifier and the reaction chamber.

13. **(Original)** The method according to Claim 1, further comprising providing the second connection point between the first connection point and the first reactant source.

14. **(Original)** The method of Claim 1, further comprising the step of maintaining the third conduit at a temperature at least equal to a condensation temperature of the first reactant.

15. **(Original)** The method according to Claim 1, further comprising the step of maintaining the second conduit at a temperature no greater than a reaction temperature of the reaction chamber.

16. **(Original)** The method according to Claim 1, wherein the third conduit is an open gas flow channel.

17. **(Original)** The method according to Claim 1, wherein the third conduit does not include valves.

18. **(Original)** The method according to Claim 1, wherein the first conduit does not include valves.

19. **(Original)** The method according to Claim 1, further comprising the steps of providing an outlet conduit for withdrawing unreacted reactants from the reaction chamber and connecting the third conduit to the outlet conduit.

20. **(Original)** The method according to Claim 1, further comprising the steps of providing an outlet conduit for withdrawing unreacted reactants from the reaction chamber and connecting the third conduit to a separate outlet conduit.

21. **(Original)** The method according to Claim 1, further comprising the steps of connecting a second inactive gas source to an inlet of the first reactant source and using inactive gas from the second inactive gas source as a carrier gas for the first reactant.

22. **(Original)** The method according to Claim 1, further comprising the steps of connecting the inactive gas source to an inlet of the first reactant source and using inactive gas from the second inactive gas source as a carrier gas for the first reactant.

23. **(Original)** The method according to Claim 1, further comprising the steps of draining substantially all of the first reactant from the reactant source through the third conduit to between the repeated alternating pulse of the first reactant.

24. **(Original)** The method according to Claim 1, further comprising the steps of providing a condensation vessel and connecting the condensation vessel to the third conduit and condensing vaporized reactant residues in the condensation vessel.

25. **(Original)** The method according to Claim 1, further comprising connecting a second inactive gas source to the third conduit via a fourth conduit and feeding inactive gas into the third conduit.

26. **(Original)** The method according to Claim 25, further comprising using the inactive gas fed into the third conduit via the fourth conduit to reduce an amount of gas withdrawn from the first conduit.

27. **(Original)** The method according to Claim 1, further comprising connecting the inactive gas source to the third conduit via a fourth conduit and feeding inactive gas into the third conduit.

28. **(Original)** The method according to Claim 27, further comprising using the inactive gas fed into the third conduit via the fourth conduit to reduce an amount of gas withdrawn from the first conduit.

29. **(Original)** The method according to Claim 28, further comprising feeding the inactive gas into the third conduit via the fourth conduit when the first reactant is being fed into the reaction chamber, wherein the inactive gas is fed during pulsing of the reactant.

30. **(Original)** The method according to Claim 1, further comprising connecting the inactive gas source to the third conduit via a fourth conduit upstream of a flow restrictor and feeding inactive gas into the third conduit.

31. **(Original)** The method according to Claim 1, further comprising feeding inactive gas into the reaction chamber in-between the repeated alternating pulses of the first reactant.

32. **(Original)** The method according to Claim 1, further comprising the steps of alternately, with respect to the first reactant, transferring a second reactant into the reaction chamber and allowing the second reactant to react with the surface of the substrate in the reaction chamber.

33. **(Original)** The method according to Claim 1, further comprising the steps of:
providing a second reactant source;
transferring a second reactant from the second reactant source to the reaction chamber via a fourth conduit;
alternately, with respect to the first reactant, allowing the second reactant to react with the surface of the substrate in the reaction chamber;
feeding inactive gas from the inactive gas source into the fourth conduit via a fifth conduit that is connected to the fourth conduit at a third connection point so as to create a second gas phase barrier between repeated alternating pulses of the second reactant entering the reaction chamber; and
withdrawing the inactive gas from said fourth conduit via a sixth conduit connected to the fourth conduit at a fourth connection point.

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ASM MICROCHEMISTRY OY

Additional name(s) of conveying party(ies) attached?

() Yes (X) No

2. Name and address of receiving party(ies):

Name: ASM INTERNATIONAL N.V.

Internal Address:

Street Address: Jan van Eycklaan 10, 3723 BC
Bilthoven, THE NETHERLANDS

Additional name(s) of receiving party(ies) attached?

() Yes (X) No

3. Nature of conveyance:

(X) Assignment
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Execution Date: (If multiple assignors, list execution dates in numerical order corresponding to numbers indicated in 1 above) November 26, 2003

4. Application number(s) or Patent number(s):

() Application(s) filed herewith Execution Date(s):

(X) Patent Application Nos and Filing Dates:
See Attached Appendix A(X) Patent Nos. and Issue Dates:
See Attached Appendix A

Additional numbers attached? () Yes (X) No

5. Name and address of party to whom correspondence concerning document should be mailed:

Name: Andrew N. Merickel
 KNOBBE, MARTENS, OLSON & BEAR, LLP
 Customer No. 20,995
 Internal Address: Fourteenth Floor
 Street Address: 2040 Main Street
 City: Irvine State: CA ZIP: 92614
 Attorney's Docket No.: ASMMC.059GEN

7. Total fee (37 CFR 1.21(h)): \$40 x 60 = \$2,400

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6. Total number of applications and patents involved: 609. Statement and signature.

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Andrew N. Merickel
Name of Person Signing

Signature

December 17, 2003
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ASSIGNMENT

WHEREAS, ASM Microchemistry OY, a Finnish corporation having offices at Kutojantie 2B, 02630 Espoo, Finland (hereinafter "ASSIGNOR"), represents that it has certain right, title and interest in the United States issued Letters Patents and applications for Letters Patents in the United States (hereinafter "the Patents and Patent Applications") recited on Appendix A, attached hereto, and in the inventions disclosed therein.

WHEREAS, ASM International N.V., a Netherlands corporation having offices at Jan van Eycklaan 10, 3723 BC Bilthoven, THE NETHERLANDS (hereinafter "ASSIGNEE") desires to purchase the entire right, title, and interest in and to the inventions disclosed in the Patents and Patent Applications;

NOW, THEREFORE, in return for good and valuable consideration, the receipt of which is hereby acknowledged, ASSIGNOR hereby further acknowledges that it has sold, assigned, and transferred, and by these presents does hereby sell, assign, and transfer, unto ASSIGNEE, its successors, legal representatives, and assigns, any right, title, and interest that ASSIGNOR has throughout the world in, to, and under the said inventions, and the said Patents and Patent Applications and all Patents that may be granted thereon, and all provisional applications relating thereto, and all divisions, continuations, reissues, reexaminations, renewals, and extensions thereof, and all rights of priority under International Conventions and applications for Letters Patent that may hereafter be filed for said inventions or for the said Patents and Patent Applications in any country or countries foreign to the United States; and ASSIGNOR hereby authorizes and requests the Commissioner of Patents of the United States, and any Official of any country foreign to the United States, whose duty it is to issue patents on applications as aforesaid, to issue all Letters Patents for said inventions and all Letters Patents resulting from the Patents and Patent Applications to ASSIGNEE, its successors, legal representatives, and assigns, in accordance with the terms of this Agreement.

ASSIGNOR does hereby sell, assign, transfer, and convey to ASSIGNEE, its successors, legal representatives, and assigns all claims for damages and all remedies arising out of any violation of the rights assigned hereby that may have accrued prior to the date of assignment to ASSIGNEE, or may accrue hereafter, including, but not limited to, the right to sue for, collect, and retain damages for past infringements of the said issued Letters Patents;

ASSIGNOR hereby covenants and agrees that it will communicate to ASSIGNEE, its successors, legal representatives, and assigns any facts known to ASSIGNOR respecting the Patents and Patent Applications immediately upon becoming aware of those facts, and that it will testify in any legal proceeding involving any of the Patents and Patent Applications, will sign all lawful papers, execute all divisional, continuing, and reissue applications, make all rightful oaths, and will generally do everything possible to aid ASSIGNEE, its successors, legal representatives, and assigns to obtain and enforce the Patents and Patent Applications in all countries.

IN TESTIMONY WHEREOF, I hereunto set my hand and seal this 26 day of November, 2003

ASM Microchemistry OY

By: T. Oller

Name Printed: ILKKA OLLER

Title: Managing Director

Mr. B. J. J.

Witness Signature

APPENDIX A

Client Code: ASMMC.059GEN

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PATENTS			
SERIAL NO.	DATE FILED	PATENT NO.	ATTN. DOCKET NO.
09/686,613	1/4/00	6,630,030	SEPP1.001CP1
09/681,020	6/7/00	6,418,577	SEPP2.001APC
09/619,820	07/20/00	6,506,352	SEPP4.001AUS
09/687,355	10/13/00	6,632,279	SEPP5.001AUS
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09/568,077	5/10/00	6,562,140	ASMMC.012AUS
09/769,662	1/25/01	6,579,374	ASMMC.012C1
09/687,204	10/13/00	6,482,262	ASMMC.026AUS
09/687,205	10/13/00	6,475,276	ASMMC.027AUS

PATENT APPLICATIONS		
SERIAL NO.	DATE FILED	ATTN. DOCKET NO.
10/645,830	8/21/03	SEPP1.001CP1C1
10/205,296	7/24/02	SEPP4.001C1
10/618,429	7/10/03	SEPP5.001C1
10/385,926	2/13/03	SEPP6.001DV1
10/205,297	7/24/02	SEPP7.001DV1
10/394,309	3/20/03	SEPP8.001C1
09/787,062	6/28/01	SEPP9.001APC
10/410,718	4/8/03	SEPP10.001C1
09/836,674	4/16/01	SEPP11.001AUS
10/270,745	10/11/02	SEPP11.001CP1
09/835,931	4/16/01	SEPP12.001AUS
09/854,706	5/14/01	SEPP14.001AUS
10/003,749	10/23/01	SEPP15.001AUS
10/066,316	1/29/02	SEPP16.001AUS
10/067,634	2/4/02	SEPP17.001AUS

APPENDIX A

Client Code: ASMMC.059GEN

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10/100,500	3/15/02	SEPP18.001AUS
10/110,598	4/11/02	SEPP19.001APC
10/110,730	4/11/02	SEPP20.001APC
10/148,525	8/27/02	SEPP21.001APC
10/276,663	11/15/02	SEPP22.001APC
10/333,521	1/17/03	SEPP23.001APC
10/263,859	9/23/02	ASMMC.002C1
10/329,658	12/23/02	ASMMC.002DV1
10/237,526	9/6/02	ASMMC.004DV1
10/303,355	11/21/02	ASMMC.4DV1C1
10/303,293	11/22/02	ASMMC.4DV1CP1
09/887,199	6/21/01	ASMMC.005AUS
10/281,418	10/25/02	ASMMC.007C1
10/049,125	2/7/02	ASMMC.008APC
10/383,291	3/6/03	ASMMC.012C2
09/997,396	11/28/01	ASMMC.020AUS
10/246,131	9/17/02	ASMMC.026C1
10/210,715	7/30/02	ASMMC.027C1
09/945,463	8/31/01	ASMMC.028AUS
10/653,737	9/2/03	ASMMC.029DV1
09/801,542	3/7/01	ASMMC.030AUS
10/227,475	8/22/02	ASMMC.031AUS
10/136,095	4/30/02	ASMMC.032AUS
10/007,304	12/5/01	ASMMC.033AUS
10/066,169	1/30/02	ASMMC.034AUS
10/187,142	6/28/02	ASMMC.035AUS
09/975,466	10/9/01	ASMMC.036AUS
10/222,005	8/14/02	ASMMC.037AUS
10/242,368	9/12/02	ASMMC.038AUS
10/285,348	10/30/02	ASMMC.042AUS

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ALD precursor chemistry: Evolution and future challenges

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Abstract: The requirements of ALD precursors differ from those of CVD concerning thermal stability, adsorption on the surface, and reactions towards each other. In the first ALD experiments in the 70s elements (Zn, Cd, S), metal halides and non-metal hydrides (H_2O , H_2S) were used. In the 80s the selection of precursors widened to metal complexes (alkoxides, β -diketonates) and simple organometallics (alkyl compounds). In the 90s both new metal (Cp-compounds, alkylamides) as well as non-metal precursors (H_2O , O, hydrazine) have been introduced. A characteristic feature of ALD is that surface groups play an important role as reactive sites for the next precursor pulse. The development of ALD precursors is limited by the small number of groups working in the field. It seems, however, that the precursor development is diverged and tailored molecules are designed for each process.

I. INTRODUCTION

Atomic Layer Deposition (Epitaxy) developed in the early 70s is a modification of CVD and can also be called as "alternately pulsed-CVD" [1,2]. Gaseous precursors are introduced one at a time to the substrate surface and between the pulses the reactor is purged with an inert gas or evacuated. In the first reaction step the precursor is saturatively chemisorbed at the substrate surface and during the subsequent purging the excess of the precursor is removed from the reactor. In the second step the other precursor is introduced on the substrate and the desired film growth reaction takes place. After that the reaction byproducts and the precursor excess are purged out from the reactor. When the precursor chemistry is favourable, *i.e.* the precursors adsorb and react with each other aggressively, one ALD cycle can be performed in less than one second in properly designed flow type reactors.

The striking feature of ALD is the saturation of all the reaction and purging steps which makes the growth self-limiting. This brings the large area uniformity and conformality, the most important properties of ALD, as shown in very different cases, *viz.* planar substrates [3], deep trenches [4] and in the extreme cases of porous silicon [5] and high surface area silica and alumina powders [6,7]. Also the control of film thickness is straightforward and can be made by simply calculating the growth cycles. ALD was originally developed to manufacture luminescent and dielectric films needed in electroluminescent displays [8] and a lot of effort has been put to the growth of doped zinc sulfide and alkaline earth metal sulfide films [9]. Later ALD has been studied for the growth of different epitaxial III-V [10,11] and II-VI [12,13] films, non-epitaxial crystalline or amorphous oxide [14,15] and nitride [16,17] films and their multilayer structures. Minor attention has been given to grow other films like those of metals and fluorides [18]. There has been considerable interest towards the ALE growth of silicon and germanium films but due to the difficult precursor chemistry the results have not been very successful [19,20].

2. REQUIREMENTS FOR THE ALD PRECURSORS

The precursors maybe gaseous, liquid or solid and in the last two cases the requirement is that they must be volatile. The vapor pressure must be high enough for effective mass transportation. The solids and some

liquids need to be heated inside the reactor and introduced through heated tubes to the substrate. The necessary vapor pressure must be reached at a temperature below the substrate temperature to avoid condensation of the precursors on the substrate.

The self-limiting growth mechanism of ALD makes it easy to use also relatively low vapor pressure precursors though their evaporation rates may somewhat vary during the process because of changes in surface area. The technologically challenging task of pulsing precursors evaporated at high temperature is solved elegantly by inert gas valving [2,3]. A challenge remaining with very small particle size solids is to prevent the particles from being transported by the carrier gas and entering the films.

The precursors must be thermally stable at the substrate temperature because their decomposition would destroy the surface control and accordingly the advantages of the ALD method. A slight decomposition, slow compared to the ALD growth, is acceptable as shown in the case of metal alkoxide precursors in the growth of oxide films [21,22].

The precursors have to chemisorb on or react with the surface. The interaction between the precursor and the surface as well as the mechanism of the adsorption is different for different precursors as will be pointed out later on. The adsorption can in the most cases be considered as an exchange reaction as reported in the growth of oxide films where the surface OH groups play an important role [23,24]. After purging, the molecule at the surface has to react aggressively with the second precursor and form the desired solid film. The demand of highly reactive precursors in ALD is in marked contrast to the selection of precursors for conventional CVD. The aggressive reactions guarantee effective use of precursors, short pulse times and purity of the films in ALD. Thermodynamic considerations of the film formation reactions are useful although the dynamic conditions in the process do not completely fulfill the real equilibrium requirements. The aggressive reaction desired means that reactions having large negative values of ΔG are looked for. Useful programs for calculations exist [25] but unfortunately thermodynamic data are not available for a large number of organometallic precursors. The ΔG value is only tentative since it tells about the spontaneity of the reaction between the gaseous precursor molecules but nothing on the kinetics and, more importantly, nothing on adsorption. If there is no site where the precursors can adsorb and be anchored, the growth can not take place. There is no thermodynamic data for calculation and prediction of adsorption and surface reactions and therefore to get predictions of them extensive quantum chemical calculations are needed. The requirement for a negative ΔG is not strict since the growth proceeds under dynamic conditions where the by-products are removed from the surface. The reaction between InCl_3 and water to In_2O_3 has been successfully utilized in ALD although its ΔG is slightly positive [26].

The side-products in the reaction must be gaseous in order to allow their easy removal from the reactor. The side-products should not further react or adsorb on the surface. The reaction between metal chlorides and water, often used in the ALD growth of oxide films, produces HCl which may readSORB or react and cause lowering of the growth rate or inhomogeneity in film thickness as shown in the case of TiO_2 , for example [23,27,28]. HCl has been shown to adsorb also on the alumina and undergo an exchange reaction between the OH group, most readily with the basic ones [29].

Precursors should not react with the film and cause etching. NbCl_5 is an extreme example since it reacts with niobium oxide and volatile oxochlorides are formed hindering the film growth [30]. TaCl_5 behaves slightly similarly but the etching is not so severe and Ta_2O_5 film can be grown in a self-limiting manner below the temperature where the etching begins, about 275°C [31].

The final requirement for the precursor is that it should not dissolve in the film. This rather rare situation was observed when copper films were grown using zinc vapor as a reducing agent. Zinc dissolved in copper forming brass. During purging and the next copper precursor (CuCl) pulse zinc was re-evaporated and an uncontrolled copper formation reaction took place [32].

While integrating ALD processes for making complete devices, the compatibility of the precursors with the underlying material, substrate or film, must be taken into account. No etching, harmful reactions or dissolution may take place.

led tubes to the substrate, substrate temperature to avoid

relatively low vapor pressure process because of changes in evaporated at high temperature by small particle size solids is entering the films.

because their decomposition would method. A slight decomposition of metal alkoxide precursors in

action between the precursor and precursors as will be pointed out change reaction as reported in the role [23,24]. After purging

and form the desired solid film to the selection of precursors for precursors, short pulse times and ion reactions are useful although

equilibrium requirements. The values of ΔG are looked for. Useless data are not available for a large

it tells about the spontaneity of kinetics and, more importantly, can be anchored, the growth can

of adsorption and surface calculations are needed. The

dynamic conditions where the and water to In_2O_3 has been

easy removal from the reactor reaction between metal chlorides which may readSORB or react and shown in the case of TiO_2 , for undergo an exchange reaction

extreme example since it reacts in growth [30]. $TaCl_5$ behaves in a self-limiting manner below

film. This rather rare situation. Zinc dissolved in copper zinc was re-evaporated and an

ability of the precursors with etching, harmful reactions of

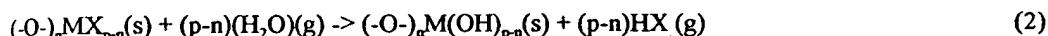
3. PRECURSOR COMBINATIONS AND SURFACE AS A REACTANT

The unique features of ALD are not that much reflected in the choices of single precursor molecules which are essentially the same as those used in CVD. Rather, it is the way how they are combined (Table 1) which makes the difference. As mentioned above, the precursors must react aggressively and completely. The difference to CVD chemistry is clear since ALD favours precursor combinations, for example trimethyl-aluminium (TMA) + water, zinc chloride + hydrogen sulfide, which in CVD can not be mixed together and introduced simultaneously into the reactor.

The surface chemistry of ALD relies on either molecular chemisorption or, perhaps more often, reaction of the incoming precursor with the functional group on the surface. Experimental evidences of the latter case have been reported in many papers on ALD oxide films using water as an oxygen precursor [17,23,24, 33,34]. There the actual reaction takes place between the OH groups on the surface and the metal precursor:



where M is a metal ion, X is a ligand, typically halide, alkoxide or alkyl. p varies depending on the metal and ligand and n varies depending on the amount of surface hydroxyl groups which in turn is a function of temperature. During the next pulse water changes the surface to a hydroxylated one:



The correlation between the amount of hydroxyl groups on the surface and the amount of metal precursors adsorbed has been shown in the experiments made on high surface area silica powder [33]. Also the low growth rate of In_2O_3 thin films, known to be deficient of surface OH groups, can be explained by the lack of reaction sites during the indium precursor pulse [34]. On the other hand, the increase of the water dose in a pulse significantly increases the growth rates of oxide films which can be understood in terms of increased hydroxyl group densities [35].

The lack of anchoring sites or functional groups can be the reason for the non-ideal results obtained for example with III-V compound and elemental (metal) films. On the other hand, ALD growth on selective sites could be utilized in selective area growth experiments by patterning the OH terminated surface and growing the film on the OH covered areas only. Crystallographically selective area growth is also possible as shown by Isshiki et al. [36,37]. They grew epitaxial III-V films and by controlling purging times they were able to deposit GaAs and GaP films either selectively on the (100) surfaces only or simultaneously on both the (100) and (111) surfaces of their (100)GaAs substrates which contained V-shaped grooves with the (111) oriented sidewalls.

Direct experimental evidences on molecular chemisorption in ALD are sparse. Real time quartz crystal microbalance (QCM) measurements can be used to monitor the relative masses of adsorbed species [38]. Most processes studied by this method involve metal chlorides and water precursors and are aimed for oxide films, and also in the studies on β -diketonato complexes water has been used as the oxygen precursor. Thus the effect of OH groups is present in the adsorption which involves partial release of the β -diketonato ligands [39,40]. Kawai and coworkers [41,42] have shown, however, that $Cu(thd)_2$ and $Ca(thd)_2$ can chemisorb on silica surface without exchange reaction via the interaction between surface oxygen atoms and C-O bonds in the complex.

4. PRECURSORS USED

The need to develop a new deposition method for electroluminescent (EL) thin film devices which require high-quality, pinhole-free dielectric and luminescent films deposited on large area glass substrates resulted in the discovery of the ALD method [8]. In the monochrome yellow-emitting EL devices $ZnS:Mn$ thin films

are used as the phosphor material. Therefore, the first experiment carried out used elemental zinc and sulfur as precursors and that is the origin of the name Atomic Layer Epitaxy. When grown on single crystal substrate at high enough temperature, real epitaxy can be obtained. Soon it turned out that molecular precursors ($ZnCl_2$, $MnCl_2$, H_2S) are more convenient to handle and films of the quality needed in EL phosphors can be achieved. For these reasons and because only a few of them are volatile enough, elements are not used as precursors, Π - VI compounds being the exceptions (Table 1). Epitaxial CdTe has been grown on (100) GaAs in a monolayer fashion at a limited temperature range (260-290 °C) and at higher temperatures 0.5 ML/cycle growth was achieved [43]. With ZnSe the process window for 1 ML/cycle is wider, viz. 240-350 °C [44]. The use of elemental zinc as a reducing agent in the ALD growth of transition metal nitrides is also worth mentioning [14,16,18].

In the following the ALD precursor chemistry is highlighted according to different precursor types. Table 1 summarizes the different precursors and reactions used in ALD without references. For detailed references the recent reviews [15,45,46] are referred to.

4.1 Precursors for non-metals

4.1.1 Oxygen

Water has been by far the mostly used precursor chemical for oxygen. It reacts fast with many metal halides and alkyls and reasonably well with metal alkoxides forming via surface hydroxyl groups oxide films as described above. Problems with water arise with β -diketonato complexes because the reaction does not occur or is slow at temperatures below 500 °C. In CVD β -diketonates have been used together with oxygen but usually the temperature has been rather high [47]. Y_2O_3 films are the only ones reported to be grown by ALD from β -diketonates ($Y(\text{thd})_3$) and O_2 with a low rate of 0.2 Å/cycle [48]. The inertness of the O_2 molecule can be explained by the double bond and accordingly all burning reactions need high temperatures. The use of ozone instead of oxygen makes the ALD growth of oxides from the β -diketonates faster but slightly non-ideal since no ALD-window can be found but the growth rate increases with increasing temperature [48,49].

H_2O_2 has been in few difficult cases (In_2O_3 , SiO_2) used instead of water to improve the growth rate [50,51]. The improvement can be explained by the increased number of OH groups on the surface. H_2O_2 reacts also with TMA more eagerly than water but at low temperatures the resulting Al_2O_3 films are not very dense as is the case also when water is used [52]. Alcohols have been used as oxygen precursor in deposition of Al_2O_3 films from both $AlCl_3$ and different alkoxides [53].

4.1.2 Sulfur and selenium

Hydrogen sulfide is a suitable and the mostly used sulfur precursor in ALD. It reacts well with very different metal precursors: halides, alkyls, carboxylates, β -diketonates and cyclopentadienyl compounds (Table 1). H_2S is used in the large scale production of ZnS based and pilot scale production of SrS based EL phosphors. Quantum chemical calculations on the reaction $ZnCl_2 + H_2S \rightarrow ZnS$ have shown that the interaction of H_2S on $ZnCl_2$ surface is dependent on the arrangement of the $ZnCl_2$ molecules. Independently chemisorbed $ZnCl_2$ molecules favour additive reaction of H_2S and the critical step is the formation of HCl while $ZnCl_2$ chains favour the immediate reaction to ZnS [54,55]. A mass-spectroscopic study of the same reaction showed that HCl is released only after the H_2S pulse and not after the $ZnCl_2$ pulse [56].

The reaction between dimethyl zinc and H_2S proceeds in a monolayer fashion at 250-310 °C [57]. The process is sensitive to H_2 purge and $Zn(CH_3)_2$ dose. It is proposed that dimethyl zinc adsorbs as a molecule on the sulfur surface. The H_2 sensitivity gives indications for the possibility of an inhibiting reaction where

ised elemental zinc and when grown on single crystal it turned out that more quality needed in EL. When enough, elements are used, elemental CdTe has been grown [56] and at higher temperatures the ML/cycle is wider, viz. 10 nm of transition metal nitrides. For different precursor types references. For detailed references.

fast with many metal halides. Hydroxyl groups oxide film because the reaction does not used together with oxygen reported to be grown [48]. The inertness of the ions need high temperatures the β -diketonates faster but increases with increasing

to improve the growth rate groups on the surface. H_2O using Al_2O_3 films are not very good precursor in deposition

acts well with very different phenyl compounds (Table 1) of SrS based EL phosphors. It is found that the interaction of H_2S with indenitely chemisorbed $ZnCl_2$ chains of HCl while $ZnCl_2$ chains same reaction showed that

on at 250-310 °C [57]. The zinc adsorbs as a molecule in inhibiting reaction where

metallic zinc and methane are formed [57]. A recent detailed study on $Cd(CH_3)_2 + H_2S$ ALE reactions showed, however, that dimethyl cadmium chemisorbs dissociatively releasing methane and forming a monomethylated surface [58]. Methane is also released during the H_2S pulse and a SH surface is formed. The mechanism proposed where the surface SH groups play an important role resembles closely to that reported for water and surface OH groups.

Hydrogen selenide reacts like hydrogen sulfide with zinc chloride and alkyl compounds forming $ZnSe$. The studies have been focused on verifying the ML growth/cycle and details of the mechanisms and the possible role of SeH groups have not been reported. The use of a thermal precursor cracker improves the film quality and has been explained by the formation of elemental species having surface mobility higher than $Zn(C_2H_5)_2$ and H_2Se [59].

4.1.3 Nitrogen

Ammonia has automatically been the precursor for nitride films. Three types of approaches have been taken towards nitride films: epitaxial GaN ($Al_{1-x}Ga_xN$, $Ga_{1-x}In_xN$) films grown from alkyl compounds and ammonia for optoelectronic applications [60], polycrystalline AlN films for dielectric and passivation layers [61] and polycrystalline transition metal nitrides (TiN , NbN , TaN , Ta_3N_5 , MoN) grown from metal chlorides for diffusion barrier and protective applications [14]. In systems where no reduction of the metal (Al , Ga , In) is needed ammonia works rather well. The impurities found from for example AlN films: chlorine and hydrogen with $AlCl_3$ [61, 62] and carbon and hydrogen with TMA [62], show that ammonia leaves behind some hydrogen. The oxygen found in the AlN films is concentrated on the surface indicating post deposition oxidation. Volatile transition metal precursors usually contain metals at their highest oxidation states but in the nitrides the oxidation state is +III and therefore reduction must occur. Ammonia is reducing in nature and for example TiN can be prepared with the reaction between $TiCl_4$ and NH_3 and the film made at 500 °C is rather pure but films of better conductivity are obtained if zinc is used as an additional reducing agent [16]. Ammonia does not reduce $TaCl_5$ and Ta_3N_5 is formed, and Zn vapour reduction is needed for TaN [63, 64]. As a summary, ammonia is a suitable precursor for nitride formation reactions with metal chlorides if the metal ion has not to be reduced. If reduction is needed an additional reducing agent may be necessary. The situation may change if other metal precursors than chlorides are used as shown in the case of TiI_4 [65].

4.1.4 Hydrides of Group V (15) Elements

PH_3 , AsH_3 , and SbH_3 are the most common precursors for the group V elements. In ALE they have been used together with both chlorides and alkyl compounds of the group III elements (Table 1). The ALE growth of the III-V compounds has not been very successful because of the complexity of the surface chemistry and there is no single mechanism for the growth of the III-V compounds by ALE. The difficulties in the surface chemistry are believed to be mainly due to the group III precursors and not because of the group V hydrides. However, the As-H species play certainly an important role in the chemisorption of TMG and the instability of surface AsH_3 is a partial reason for the problems. Fast injection of AsH_3 , high hydrogen partial pressure and injection of atomic hydrogen on AsH_3 surface have improved the self-limiting type growth [45]. However, in some experiments wide temperature, pulse time and pressure windows have been observed [66] and they must be addressed to the ligand exchange reactions similar to those described for the growth of oxide films. The precursors for the group V elements are not under special development but the users are satisfied to the compounds commercially available for MOVPE.

4.1.5 Fluorine

The only paper existing on the ALD of fluoride films reports the use of NH_4F as a precursor for $\text{Ca}_x\text{Si}_{1-x}\text{Zn}$ fluorides [67]. The precursor is not ideal and the growth rate remains low. In deposition of $\text{Si}_x\text{Ge}_{1-x}$ fluoride codoping has been performed by benzoyl fluoride which is a suitable precursor for codoping but not for growing bulk fluoride films [68].

4.2 Metal precursors

4.2.1 Halides

Metal halides, especially chlorides, are applicable precursors in ALD deposition of oxide, sulfide and nitride films. They are volatile and reactive enough but most of them are solids which is in microelectronic industry considered as a disadvantage. The ALD surface chemistry of chlorides has been studied thoroughly both on planar substrates and on high surface area oxide powders in preparation of oxides. As described above in those cases metal chlorides are reacting with surface OH groups and HCl is formed. Much less is known on the chemisorption on sulfur surfaces. The calculations show that ZnCl_2 adsorbs on sulfur surface form a stable complex [54,55] though desorption of ZnCl_2 may occur easily [56]. Due to the size of the chloride anions and their repulsion, maximum surface coverage can be either $1/3$ or $1/2$ depending on whether the adsorption mode is independent or chain-like, respectively. Experimentally it has been shown that 2-3 cycles are needed for one monolayer depending on the experimental conditions [69]. The role of surface SH groups has not been studied in detail.

The behaviour of aluminium, gallium and indium trichlorides in the growth of oxide films differs from each other markedly: Al_2O_3 can be grown with a good rate, Ga_2O_3 does not grow at all, In_2O_3 grows with a low rate. The oxide formation reactions become thermodynamically more unfavored in the same order. Partially those behaviours can possibly be addressed to the stability of OH groups on the oxide surface. The reactivity of Al, Ga and In chlorides with ammonia follows the same trend as that with water. In GaAs ALE GaCl has been more often studied as a precursor than GaCl_3 . The reaction between GaCl and AsH_3 is not very favorable and long pulsing times are needed, and on the other hand GaCl desorption may occur and GaCl surface may change to inert Ga surface [70]. The studies have shown that GaCl reacts with As_4 precursor only in the presence of hydrogen [71]. A rather wide 1 ML/cycle ALE window has been found for $\text{GaCl}_3 + \text{AsH}_3$ and the suggestion for the reaction mechanism goes via AsH and $\text{As}-\text{GaCl}_3$ surface species [72].

SiCl_4 reacts with water producing SiO_2 films. The reaction is, however, very slow and pulse times of tens of seconds are needed. The process relies on the surface OH groups and the growth rate is dependent on temperature which further determines the OH content on the surface [73]. The reaction can be enhanced by pulsing pyridine after each reactant pulse. Both the reaction temperature and pulse times could be reduced significantly without losing the growth rate per cycle and the quality of the film [74].

4.2.2 Alkyl compounds

Because of the importance of the III-V semiconductors most ALE and ALD studies using alkyl precursors deal with Ga, Al and In. Both trimethyl and triethyl compounds are easily available and their chemistry in CVD is known. No special precursor for ALE has been designed. The ALE deposition of GaAs has been studied by numerous groups using different experimental set-ups and very different results have been reported. The difficulties arise from the instability of Ga alkyl compounds (mainly trimethyl gallium, TMG). In ultra high vacuum systems no saturative growth or a very narrow temperature range for the saturation

has been observed but the saturation can be enhanced by laser irradiation [45]. The use of high-speed flow in a hydrogen transport has resulted in reasonably wide saturation range [66,75].

Three models have been suggested for the ALE GaAs surface chemistry. First, the TMG converts the arsenic-terminated surface to a gallium-terminated one and the methyl groups desorb. This surface is no longer reactive towards TMG [76]. Second, TMG reacts with arsenic surface and forms a gallium rich surface covered with methyl groups. The methyl groups make the surface passive for further adsorption of TMG [77]. Third, TMG (or TEG) decomposes on the surface to a monomethyl (ethyl) species which desorbs from the surface and no deposition takes place. The growth requires a flux balance between the adsorbing and desorbing species [78]. As a conclusion it can be said that ideal saturative growth is hard to achieve by TMG (TEG) and arsine.

The behaviours of Al and In alkyls are similar to those of gallium alkyls in the growth of the III-V compounds. AlAs and InP are the most commonly studied materials after GaAs. By using different tricks in time scales, flow rates, precursor cracking, and H₂ purges it has been possible to grow these materials 1 ML/cycle in a limited temperature range [45]. In the growth of oxide films the alkyl compounds behave like chlorides: TMA + H₂O is almost an ideal reaction [79,80], TMG + H₂O does not proceed at all and TMI + H₂O shows extremely low growth rate [34]. TMA-water process works in a wide temperature range (100-500 °C) but the OH (or H) content of the film increases with decreasing temperature. The process has been studied in many applications including modification of catalyst supports and membranes [81], dielectric films for EL devices and corrosion protection films. The reaction of Al and Ga alkyl compounds with ammonia results in AlN and GaN [60,62]. Clear temperature window for the self-limiting growth does not exist but stable growth can be achieved at fixed temperature.

Dimethyl (DMZ) and diethyl (DEZ) zinc have been used in deposition of both epitaxial ZnS and ZnSe films as well as polycrystalline ZnS and ZnO films. Close to 1 ML/cycle growth was observed in the reaction between DMZ and H₂S at 25-500 °C [82]. The process can also be used in a large scale to fabricate ZnS:Mn based EL devices [83]. Both DMZ and DEZ react vigorously with water forming ZnO at 100-250 °C the ALD growth rate being reaction temperature dependent [84]. This and the observation that the reactions between DMZ and H₂S and H₂Se are hydrogen pressure dependent indicate thermal instability of the zinc alkyl compounds, not to forget the role of surface OH, SH and SeH groups, however. If the decomposition is complete and a zinc surface is formed, the chalcogenide formation reaction is inhibited.

4.2.3 Alkoxides

Alkoxides which are well known precursors in CVD have only in a few cases used in ALD (Table 1) to grow oxide films. Water and alcohols have served as oxygen precursors [21,53]. Alkoxides have a tendency to decompose at high temperatures and therefore ALD processes are limited to temperatures below 400 °C where the growth is an ALD-type exchange reaction utilizing surface OH groups. The size of the precursor molecules affects the growth rate and in the case of TiO₂ the precursor affects also the crystallinity [21,85]. Alkoxides are very important precursors for Nb and Ta oxides because their chlorides etch the forming oxides [86,87].

4.2.4 β -diketonato complexes

Electropositive metals have not many volatile compounds and β -diketonato complexes are among the few ones. The need of volatile alkaline earth and rare earth metal compounds for CVD deposition of high temperature oxide superconductors boosted the studies on β -diketonato complexes. In ALD the main interest has been in deposition of SrS based EL phosphors and thd-chelates (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione) are used as the precursors [88]. The instability of the precursors may cause some thickness non-uniformity for the films and the difficulties increase in the series Ca < Sr < Ba [89]. Anyway, Sr(thd)₂ is used in a pilot scale for SrS EL films [90].

The alkaline earth β -diketonato complexes may oligomerize which limits the volatility and the neutral adducts have been added to the complexes to keep them monomolecular. The complexes age by reacting with moisture also resulting in oligomers. The adduct molecules are believed to be more stable against aging as well [47,91]. ALD depositions of alkaline earth sulfide films have been carried out using adducted thd complexes but it seems that the neutral adduct molecules do not stay intact at the temperatures [92,93]. Thus the surface reaction is basically the same as in the case of non-adducted complexes. One other way to avoid the aging and possible decomposition of the β -diketonato complexes is to make them *in situ* in the ALD reactor. This is possible by introducing Hthd liquid vapor over heated alkaline earth metal or hydroxide and a reasonable growth rate (0.8-1 Å/cycle) can be achieved [94]. The vaporization of the Hthd liquid inside the ALD reactor requires careful temperature control but this can be avoided by pulsing Hthd from outside of the ALD reactor [95].

As mentioned above the ALD deposition of oxide films from β -diketonato complexes and water is not a favourable reaction the deposition of MgO being an exception but with a low deposition rate [96]. These results have been obtained by using ozone as an oxygen precursor. Even ternary LaCoO₃ and LaNiO₃, which usually are difficult to prepare by CVD techniques have been grown by ALD from the corresponding thd complexes and ozone [97,98].

Cu(thd)₂ is a possible precursor for deposition of metallic copper. The reduction is made by H₂ and due to the instability of the precursor the process is self-limited only in the temperature range 190 to 260 °C. The initiation of the growth is not straightforward and a Pt/Pd seed layer is needed [99,100]. Cu(thd)₂ as well as many rare earth thd-chelates have been employed as precursors for doping ZnS or SrS based EL phosphor films [101].

The adsorption of several transition metal thd-complexes on high surface area powders have been studied in detail [102]. In adsorption on oxide surface the thd-chelate undergoes an exchange reaction between the surface OH groups. The number of metal atoms on the surface is a function of the OH group concentration (calcination temperature) and the size of the molecule. There is one recent example of molecular adsorption of a β -diketonate chelate on silica surface, *viz.* Cr(acac)₃ (Hacac = 2,4-pentanedione). The molecular adsorption occurs only at a limited temperature range 160-200 °C, however [103].

4.2.5 Cyclopentadienyl compounds

Magnesium and few other cyclopentadienyl (Cp) compounds are known as oxide precursors in CVD. Also some metal films have been grown by CVD from the cyclopentadienyl compounds. In ALD the first report on these precursors is that of Huang and Kitai [104] on MgO films. Our interest towards the Cp compounds stems from the need to find volatile compounds for the heavier alkaline earth metals capable to react with water to oxide at reasonable temperatures. Because the experiments with β -diketonates failed Cp compounds, though considered to be very sensitive to oxygen and moisture, were chosen. In practice, however, these compounds turned out to be more stable than expected and could even be shortly exposed to air. Not much attention has been paid on the growth of binary oxide (SrO, BaO) films but more importantly ternary SrTiO₃ and BaTiO₃ compounds were grown with Ti alkoxide as a titanium source. The depositions on glass substrate follow the principles of ALD: the films are polycrystalline, the composition can be affected by changing the pulse ratio of the metal precursors, thickness is uniform and depends linearly on the number of the growth cycles, and the conformality of the films is perfect [105]. Cp compounds form a big family of precursors since the ligands can be varied by substitutions in the carbon 5-ring, largening the ring system (indene, fluorene) and by linking two ring systems together by a bridge. The potential of the Cp compounds as precursors for alkaline earth metals is still largely unknown. Metallocenes of the group IV metals (Ti, Zr, Hf) are well-known in polyolefin catalysis and they are volatile compounds which react readily with water. Thus, these are also potential ALD precursors for TiO₂, ZrO₂ and HfO₂ films.

Sr((i-prop)₃Cp)₂ reacts also with H₂S forming SrS film. The benefit of this precursor is that temperatures below 200 °C can be used to fabricate crystalline films with high growth rates [106]. In luminescent EL films

its low volatility and high molecular. The complexes in the molecules are believed to have been carried on and do not stay intact at all in the case of non-additive of the β -diketonato complex by introducing Hthd with rate (0.8-1 Å/cycle) and requires careful temperature actor [95].

to complexes and water and position rate [96]. The only LaCoO_3 and LaNiO_3 which from the corresponding

duction is made by H_2 and temperature range 190 to 260 °C is led [99,100]. $\text{Cu}(\text{thd})_2$ as well as ZnS or SrS based EL phosphor

ea powders have been studied exchange reaction between the OH group concentration. Example of molecular adsorption (pentanedione). The molecular

xide precursors in CVD. Also bounds. In ALD the first report towards the Cp compounds of metals capable to react with β -diketonates failed. Cp, were chosen. In practice could even be shortly exposed (SrO, BaO) films but more xide as a titanium source. The polycrystalline, the composition uniform and depends linearly [105]. Cp compounds form a carbon 5-ring, largening the ridge. The potential of the Cp. Metallocenes of the group 4 compounds which react readily and HfO_2 films. precursor is that temperatures [106]. In luminescent EL films

a dopant is needed and when an organometallic precursor for the dopant is a necessity, the growth temperature must be low and then the alkaline earth Cp-precursors may be a good choice.

Rare earth metals form another group of electropositive metals which have only a few volatile compounds. The rare earth β -diketonates are reasonably stable and their volatility properties are good but their reactivity with water to oxide films is low. As dopant precursors for ZnS:Ln and SrS:Ln films they can be used [101]. However, with cerium, one of the most important dopants for SrS , better results have been obtained with Cp precursors [83].

4.2.6 Carboxylato complexes

The number of known volatile carboxylato complexes is low. In ALD only zinc acetate has been used in deposition of ZnS films [107]. Zinc acetate oligomerizes to a tetramer before evaporation and the actual molecule adsorbing on the surface is $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$ and accordingly the growth rate of the film is high [106,108]. Zinc acetate can be used also as a precursor for ZnO films although the growth rate is very low.

4.2.7 Silanes and germanes

ALE deposition of silicon (and also germanium) using different silanes or chlorosilanes has extensively been studied. Special attention has been given to the adsorption of different precursors on Si surface [19,20]. The results show that the surface chemistry of the precursors used is not favourable but UV-irradiation or thermal cycling is needed for obtaining pure films. According to Gates [109] all reactions studied in ALE using two Si precursors, silane + chlorosilane, are thermodynamically unfavoured. Only those reactions which involve atomic hydrogen are spontaneous and can be considered self-limiting. It seems that reactants which can be alternately pulsed and which make the self-limiting Si growth possible are not yet known.

4.2.8 Others

There are few other precursors not mentioned above which have been used in ALD. Alkylamides, recently widely studied in CVD, have only a few times been used in ALD [110]. Isocyanate compounds of silicon ($\text{Si}(\text{NCO})_4$) form a new interesting group of precursors with which it is possible to grow SiO_2 films in a ML/cycle fashion [111,112]. The pulse times have, however, been unpractical long like in the case of SiCl_4 . The development of these new precursors shows that new potential ALD precursors can be found.

5. FUTURE CHALLENGES

There are a lot of challenges and development work to be done before ALD is accepted as an important thin film deposition technology for opto- and microelectronics. As pointed out above the key role in the process development is the precursor chemistry. The first challenge is to get more chemists to work with the precursors. CVD faces the same challenge because worldwide the precursor development is not very extensive. On the other hand, there are of course more companies specializing on CVD precursors than ALD precursors. Luckily, these companies have shown increasing interest towards ALE and ALD which is a natural development recognizing the similarities of the two fields.

The areas where ALD precursor development is needed are obvious: areas where the experiments with chemicals available have not been very successful, *viz.* III-V compounds and silicon. The other areas where

precursor development is needed are at least: good reducers for reactions where oxidation states might be lowered, more efficient nitrogen source material than ammonia, new organometallic precursors, electropositive elements, stable volatile precursors for noble metals, and suitable reactant combinations for metal film depositions.

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[109] G.
[110] M.
[111] S.
[112] N.

Table 1

Metal

Elem.

An

Cd

Hali

Alc

Gor

Gia

Br

Li

S

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Table I. Precursors used in ALD technique. For references see the recent review papers [14,15,45,46].

Metal precursor type	Non-metal precursor	Film material grown	
		Elements	Compounds
In	S Se Se(C ₂ H ₅) ₂ Te	ZnS ZnSe ZnSe ZnTe CdS CdTe	
Cd	S Te		
Halides			
AlCl ₃	H ₂ O, H ₂ O ₂ , O ₂ , ROH NH ₃ AsH ₃ P ₂ O ₅ (CH ₃ O) ₃ PO	Al ₂ O ₃ AlN AlAs AlPO ₄ AlPO ₄ GaAs GaP _{1-x} As _x	
GaCl	AsH ₃ P ₄ + As ₄	GaN	
GaCl ₃	NH ₃ AsH ₃ CuCl + H ₂ S	GaAs CuGaS ₂ InP	
InCl	PH ₃ GaCl + AsH ₃ H ₂ O, H ₂ O ₂	In _{1-x} Ga _x As In ₂ O ₃ In ₂ S ₃	
InCl ₃	H ₂ S H ₂ O	SiO ₂ Cl dopant in SrS	
SiCl ₄	H ₂ S Si ₂ H ₆	Si	
Si ₂ Cl ₆	H ₂ O	TiO ₂	
TiCl ₄	NH ₃	TiN	
TiI ₄	NH ₃ H ₂ O, H ₂ O ₂ H ₂ O	TiN	
ZrCl ₄	H ₂ O	TiO ₂	
HfCl ₄	H ₂ O	ZrO ₂	
NbCl ₅	NH ₃	HfO ₂	
TaCl ₅	H ₂ O NH ₃	NbN	
	NH ₃ + Zn	Ta ₂ O ₅	
	NH ₃ + H ₂ O	Ta ₃ N ₅	
	NH ₃ + Zn	Ta ₃ N	
MoCl ₆	H ₂ O	TaO _x N _y	
WOCl ₆	H ₂ S	MoN	
MnCl ₂		WO ₃	
		Dopant in ZnS	

CuCl	Zn, H_2	Cu
	$\text{GaCl}_3 + \text{H}_2\text{S}$	CuGaS_4
ZnCl_2	H_2S	ZnS
	H_2Se	ZnSe
	$\text{H}_2\text{S} + \text{Se}$	$\text{ZnS}_{1-x}\text{Se}_x$
CdCl_2	H_2S	CdS
SnCl_4	H_2O	SnO_2
SbCl_3	H_2O	Sb_2O_3

Alkyl compounds

$\text{Al}(\text{CH}_3)_3$	$\text{H}_2\text{O}, \text{H}_2\text{O}_2, \text{O}_2, \text{N}_2\text{O}$	Al_2O_3
	NH_3	AlN
	AsH_3	AlAs
	$(\text{CH}_3)_2\text{N}_3\text{As}$	AlAs
$\text{Al}(\text{CH}_3)_2\text{Cl}$	H_2O	Al_2O_3
	NH_3	AlN
$\text{Al}(\text{CH}_3)_2\text{H}$	PH_3	AlP
	AsH_3	AlAs
$\text{Al}(\text{C}_2\text{H}_5)_3$	AsH_3	AlAs
	H_2O	Al_2O_3
	NH_3	AlN
$\text{Al}(\text{i-C}_4\text{H}_9)_3$	AsH_3	AlAs
$\text{Ga}(\text{CH}_3)_3$	PH_3	GaP
	AsH_3	GaAs
	BuAsH_2	GaAs
$\text{Ga}(\text{C}_2\text{H}_5)_3$	NH_3	GaN
	PH_3	GaP
	AsH_3	GaAs
	BuAsH_2	GaAs
	$(\text{CH}_3)_2\text{N}_3\text{As}$	GaAs
$\text{Ga}(\text{C}_2\text{H}_5)_2\text{Cl}$	AsH_3	GaAs
$\text{Ga}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$	AsH_3	GaAs
$\text{In}(\text{CH}_3)_3$	PH_3	InP
	AsH_3	InAs
	H_2O	In_2O_3
$\text{In}(\text{CH}_3)_2\text{Cl}$	AsH_3	InAs
$\text{In}(\text{C}_2\text{H}_5)_3$	AsH_3	InAs
$\text{In}(\text{C}_2\text{H}_5)_2\text{Cl}$	AsH_3	InAs
$\text{In}(\text{C}_2\text{H}_5)(\text{CH}_3)_2$	NH_3	InN
$\text{Zn}(\text{CH}_3)_2$	H_2O	ZnO
	H_2S	ZnS
	$\text{H}_2\text{S} + \text{O}_2$	$\text{ZnO}_{1-x}\text{S}_x$
	H_2Se	ZnSe
	$\text{H}_2\text{S} + \text{H}_2\text{Se}$	$\text{ZnS}_{1-x}\text{Se}_x$
	$(\text{C}_2\text{H}_5)_2\text{Te}$	ZnTe
	$\text{CH}_3(\text{allyl})\text{Te}$	ZnTe
$\text{Zn}(\text{C}_2\text{H}_5)_2$	H_2O	ZnO
	H_2S	ZnS
$\text{Cd}(\text{CH}_3)_2$	H_2S	CdS
	$(\text{C}_2\text{H}_5)_2\text{Te}$	CdTe
	$(\text{Pr})_2\text{Te}$	CdTe
	$\text{CH}_3(\text{allyl})\text{Te}$	CdTe
$\text{Cd}(\text{C}_2\text{H}_5)_2$	H_2S	CdS
$\text{Sn}(\text{CH}_3)_4$	NO_2	SnO_2
$\text{Sn}(\text{C}_2\text{H}_5)_4$	NO_2	SnO_2

EUROCVD 12

Alkoxides

$Al(OCH_3)_3$	H_2O	Al_2O_3
$Al(OCH(CH_3)_2)_3$	H_2O, ROH	Al_2O_3
$Ti(OCH_3)_4$	H_2O	TiO_2
$Ti(OCH(CH_3)_2)_4$	H_2O	TiO_2
$Nb(OCH_3)_5$	H_2O	Nb_2O_5
$Ta(OCH_3)_5$	H_2O	Ta_2O_5
$Pb(OBu')_2$	NH_3	TaO_3N
$Pb_2O(OBu')_6$	H_2S	PbS
	H_2S	PbS

 β -diketonato complexes

$Mg(thd)_2^*$	H_2O, O_2	MgO
	H_2S	MgS
	H_2S	CaS
$Ca(thd)_2$	NH_4F	CaF_2
	H_2S	SrS
$Sr(thd)_2$	NH_4F	SrF_2
	O_2	$SrO (SrCO_3)$
	$Ti(O^{\prime}Pr)_4 + O_2$	$SrTiO_3$
$Ba(thd)_2$	H_2S	BaS
$Y(thd)_3$	O_2, O_2	Y_2O_3
$La(thd)_3$	H_2S	La_2S_3, La_2O_2S
	$Co(thd)_2 + O_2$	$LaCoO_3$
	$Ni(thd)_2 + O_2$	$LaNiO_3$
$Ce(thd)_4$	O_2	CeO_2
$Mn(thd)_3$	H_2S	$Dopant in ZnS$
$Co(thd)_2$	O_2	Co_3O_4
$Cu(thd)_2$	H_2	Cu
	H_2S	$Dopant in SrS$
$Pb(thd)_2$	H_2S	PbS
$Ln(thd)_3^b$	H_2S	$Dopants in SrS and ZnS$

*thd = 2,2,6,6-tetramethyl-3,5-heptanedione. Alkaline earth thd-complexes used may also contain a neutral adduct molecule or they may have been slightly oligomerized

^bLn = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Tm

Cyclopentadienyl compounds

$Mg(Cp)_2^c$	H_2O	MgO
	$Al(C_5H_5)_2 + H_2O$	$MgAl_2O_4$
$Sr((i\text{-}prop)_3Cp)_2$	$Ti(O^{\prime}Pr)_4 + H_2O$	$SrTiO_3$
$Ba((CH_3)_3Cp)_2$	$Ti(O^{\prime}Pr)_4 + H_2O$	$BaTiO_3$
$Mn(Cp)_2$	H_2S	$Dopant in ZnS$
$Mn(CH_3Cp)(CO)_2$	H_2S	$Dopant in ZnS$
$ZrCp_2Cl_2$	O_2	ZrO_2
$Ce(Me_4Cp)_2$	H_2S	$Dopant in SrS$

^cCp = C_5H_5

Carboxylates

$Zn(CH_3COO)_2$	H_2S	ZnS
	H_2O	ZnO
$Zn_2(CH_3COO)_6$	H_2S	ZnS
	H_2O	ZnO

Hydrides

$(CH_3)_3NAIH_3$	NH_3	AlN
$(C_2H_5(CH_3)_2N)AlH_3$	AsH_3	AlAs
SiH_4	AsH_3	AlAs
SiH_2Cl_2	UV-light	Si
	H_2 , atomic H	Si
	C_2H_2	SiC
	NH_3 + plasma	Si_3N_4
Si_2H_6	N_2H_4	Si_3N_4
	UV-light	Si
	C_2H_2	SiC
Si_3H_8	SiH_2Cl_2 , H_2 , atomic H	Si
$(C_2H_5)_2SiH_2$	heat	Si
GeH_4	UV-light	Ge
$Ge(CH_3)_2H_2$	atomic H	Ge
$Ge(C_2H_5)_2H_2$	heat	Ge

Alkylamides

$Ti(N(CH_3)_2)_4$	$NH_3 + SiH_4$	$Ti_xSi_3N_x$
$Ti(N(C_2H_5CH_3)_2)_4$	NH_3	TiN
$Ce(N(Si(CH_3)_3)_2)_3$	H_2S	Dopant in SrS

Others

$Si(NCO)_4$	H_2O	SiO_2
$CH_3OSi(NCO)_3$	H_2O_2	SiO_2
$Pb((C_2H_5)_2NCS)_2$	H_2S	PbS

United States Patent [19]

[19]

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[11]

4,066,481

Jan. 3, 1978

[54] **METALORGANIC CHEMICAL VAPOR DEPOSITION OF IVA-VIA COMPOUNDS AND COMPOSITE**

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[73] Assignee: Rockwell International Corporation, El Segundo, Calif.

[21] Appl. No.: 647,222

[22] Filed: Jan. 7, 1976

Related U.S. Application Data

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abandoned.

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[52] U.S. Cl. 148/174; 136/89 TF;
156/610; 156/613; 156/614; 148/175; 252/62.3
S; 252/62.3 V; 357/4; 357/16; 357/30;
423/508; 423/509; 427/87; 427/90; 427/91;
427/248 B

[58] Field of Search 148/175, 174; 156/610,
156/612-614, 600, DIG. 72, 85; 252/62.35 V;
427/87, 90, 91, 248; 357/4, 16, 30; 423/509;
509; 136/89

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Primary Examiner—L. Dewayne Rutledge

Assistant Examiner—W. G. Saba

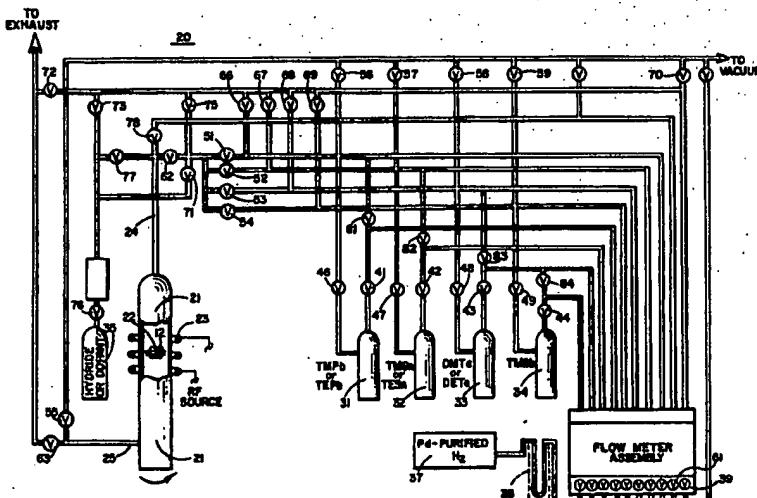
Attorney, Agent, or Firm—H. Fredrick Hamann; G. Donald Weber, Jr.; Robert Ochis

[57] ABSTRACT

A composite comprising a monocrystalline substrate and one or more layers or films of monocrystalline IVA-VIA compounds and/or alloys formed thereon by a chemical vapor deposition process. The composite is formed at a preferred temperature range of approximately 450°-650° C. The IVA-VIA layer(s) are produced by the pyrolysis of a gas mixture containing metalorganic compounds. Where single crystal metallic oxide substrates of rhombohedral structure, such as sapphire, (α -Al₂O₃), or of cubic structure, such as magnesium aluminate (spinel), are used for the growth of monocrystalline lead-containing films such as Pb_{1-x}Sn_xTe, a nucleation layer of lead is preferably formed on the substrate prior to the pyrolysis of the mixed gaseous reactants.

Using the present process, epitaxial monocrystalline IVA-VIA compounds and/or alloys can be grown on inorganic metal oxide substrates, such as cubic and rhombohedral oxides, on alkali halides and IIA fluorides, and on II-VI and III-V compounds. The compositions of the films can be varied without removing the composites from the deposition apparatus by changing the ratio of the reactant gases and the reaction temperature. The conductivity type (n-type or p-type) of the films also can be controlled without removing the composites from the deposition apparatus by varying the reactant gas compositions and by incorporating a dopant into the reactant mixtures prior to pyrolysis.

15 Claims, 3 Drawing Figures



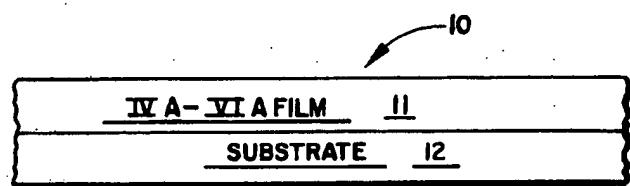


FIG. 1

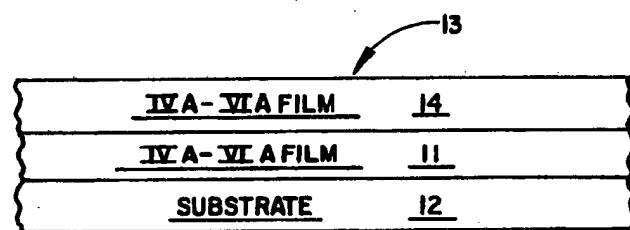


FIG. 2

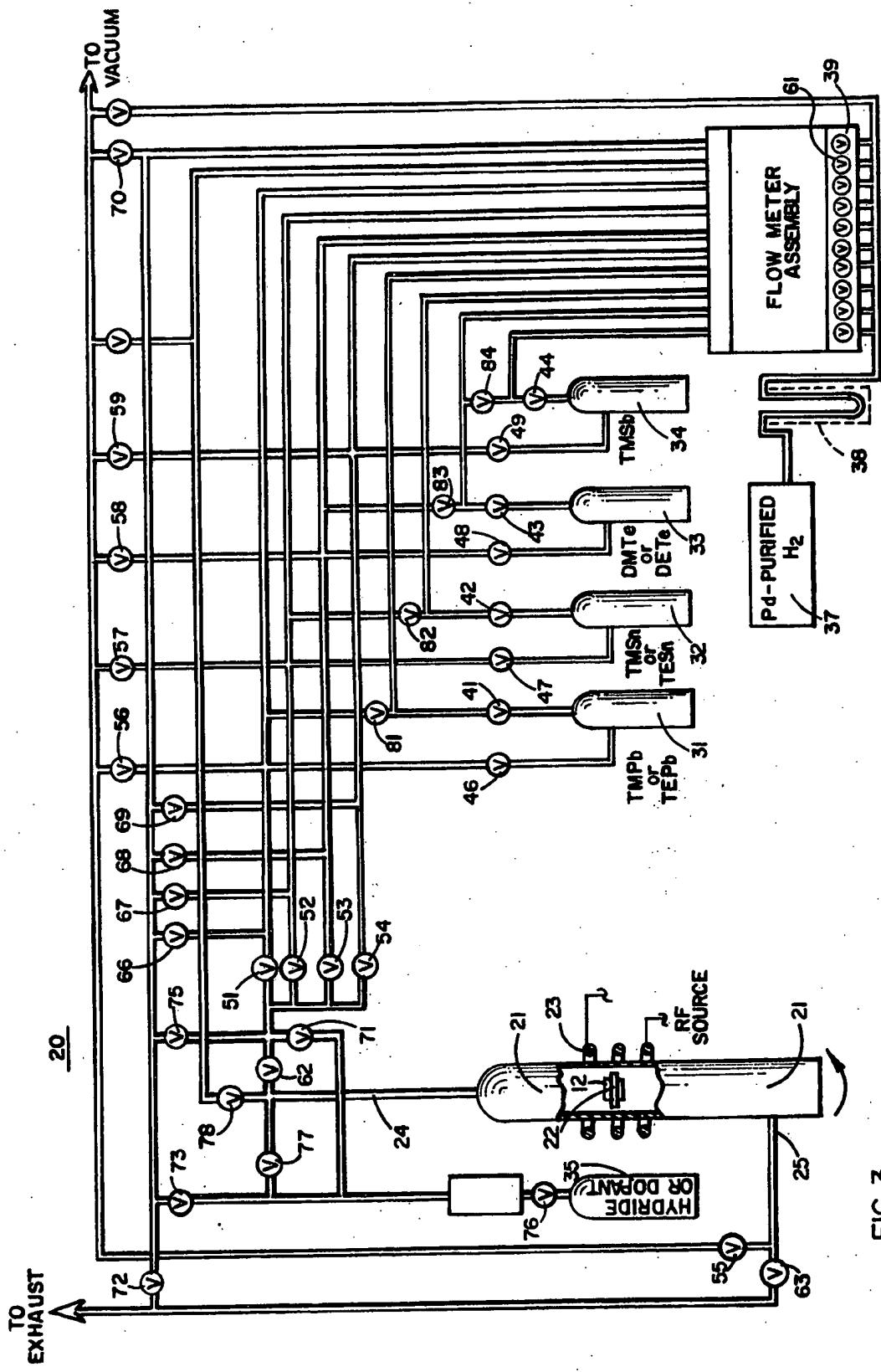


FIG. 3

METALORGANIC CHEMICAL VAPOR
DEPOSITION OF IVA VIA COMPOUNDS AND
COMPOSITE

The invention described herein was made in the course of or under contract or subcontract thereunder with the Department of the Army.

This is a division, of application Ser. No. 523,599 filed Nov. 11, 1974, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the growth of IVA-VIA compounds and, more particularly, to the growth of composites comprising layers of IVA-VIA compounds and alloys on substrates.

2. Description of the Prior Art

One application of IVA-VIA compounds is to infrared (IR) detectors. To date, various semiconductor materials have been used to form IR detectors, with the result that such detectors presently cover a wide range of the IR spectrum. However, past efforts have been concentrated on extrinsic semiconductors, rather than intrinsic semiconductors, because of the highly advanced technology for these materials, which is primarily the result of transistor technology.

While detectors formed from extrinsic semiconductors can exhibit high D^* and high speed, they are generally limited to operation at very low temperatures. Also, a relatively large volume of detector material is usually required in order to absorb sufficient incident radiation for detection. In addition to the obvious restrictions on the miniaturization of detector arrays and the accompanying signal processing circuitry, this large volume causes radiation hardening problems.

In principle, compound semiconductor materials, which are used for most intrinsic detectors, have all the advantages of the elemental (extrinsic) semiconductors and very few of the disadvantages. $Pb_{1-x}Sn_xTe$ (lead tin telluride) and $PbTe$ (lead telluride; $x=0$) are examples of excellent compound/alloy detectors for long wavelength IR. Lead tin telluride, for example, has several advantageous characteristics. Because of its direct energy gap, lead tin telluride does not require impurity to absorb incident photons, with the result that there are additional 10^4cm^{-3} available sites for capturing incident signals. Satisfactory operation with relatively thin detector films on the order of $10\text{ }\mu\text{m}$ thickness is thus possible. Also, the composition of lead tin telluride can be altered for tuning to the desired portion of the IR spectrum. A composition of approximately $Pb_{0.8}Sn_{0.2}Te$ ($x = 0.2$) is particularly useful because junction-type photovoltaic detectors using films of this composition provide peak response to infrared radiation in the $10\text{--}12\text{ }\mu\text{m}$ region.

Some growth techniques which have been used successfully for the formation of single crystal IVA-VIA compounds and alloys on other IVA-VIA compounds and alloys have not been successfully applied to insulating substrates. For example, liquid phase epitaxy (LPE) has not been reported in the growth of IVA-VIA compounds on insulators such as the alkali halides and oxide insulators, presumably because of problems in properly nucleating the IVA-VIA material. Yet there are considerable reports of the use of evaporation and sputtering for growing IVA-VIA materials on insulating halide substrates. This area is reviewed by H. M. Manasevit in *J. Crystal Growth*, vol. 22, pg. 125 et seq. (1974). It

should be noted that these processes lead to slow growth rates on insulators, typically less than about $350\text{ }\text{A}/\text{min.}$ (0.035 micron/min.). This is particularly disadvantageous and impractical for applications where thick films may be required, as in IR detectors. In addition, the composition of the grown film may not be homogeneous, particularly for alloy growth, because the vapor pressures of the source materials are different at a given temperature and must be controlled carefully to produce a film of a desired composition when two or three sources and multi-temperatures are used. Also, the composition of the vapor may differ considerably from that of the source during the evaporation process, since the vapor may consist of elements together with compounds having stoichiometry different from the source, thereby resulting in deposits of non-stoichiometric composition.

As may be thus appreciated, it is highly desirable to have a process which provides (1) a fast rate of growth for IVA-VIA compounds on substrates, (2) multilayer film structures of different compositions and impurity levels and conductivity type without removing the structures from the growth system and (3) large area films of controlled compositions and stoichiometry.

SUMMARY OF THE INVENTION

The instant invention concerns a composite comprising at least one monocrystalline layer or film of IVA-VIA compound or alloy, such as $PbTe$, $Pb_{1-x}Sn_xTe$, PbS , $PbSe$ and $SnTe$, on a monocrystalline inorganic cubic or rhombohedral oxide substrate and a chemical vapor deposition process for forming both monocrystalline and polycrystalline composites. The chemical vapor deposition process utilizes the pyrolysis of a gaseous mixture of IVA-containing metalorganic compounds and VIA-containing metalorganic compounds and/or hydrides on the substrate at a temperature preferably within the range $450\text{--}650^\circ\text{C}$. Below about 450°C film growth rates were found to be quite low; above about $550\text{--}650^\circ\text{C}$, film deterioration was usually observed on substrates such as $NaCl$ that were not stable at these temperatures. If the film contains lead and the substrate is sapphire or magnesium aluminate (spinel), a layer of lead is preferably formed first on the substrate by pyrolysis of a lead-containing metalorganic compound, followed by pyrolysis of the VIA-containing compounds and then by pyrolysis of appropriate mixtures of IVA- and VIA-containing metalorganic compounds.

By varying the deposition parameters, or by introducing impurities into the gaseous atmosphere, the film conductivity-type is controlled. Composites comprising multilayer films are formed without removing the composite from the deposition system.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partial, cross-sectional view of a IVA-VIA composite embodying principles of the present invention.

FIG. 2 is a partial, cross-sectional view of an alternative composite embodying principles of the present invention comprising multilayer films of IVA-VIA compounds.

FIG. 3 is a schematic diagram of a reactor system for forming IVA-VIA composites, such as those of FIGS. 1 and 2, in accordance with the method of the present invention.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

Referring to FIG. 1, there is shown a cross-sectional view of a composite 10 which may be formed according to the method of the present invention. The composite 10 comprises a monocrystalline layer or film 11 of compounds or alloys of groups IVA and VIA of the Periodic Table, such as PbS, PbTe, PbSe, Pb_{1-x}Sn_xTe and SnTe, epitaxially formed on a monocrystalline substrate 12 such as a semiconductor material or insulative material.

Referring now to FIG. 2, there is shown a cross-sectional view of a multilayer composite 13 which also may be grown according to the method of the present invention. Typically, the composite 13 comprises the substrate 12, an epitaxial monocrystalline layer or film 11 of lead tin telluride or lead telluride, which is of one conductivity type (such as n-type), formed on the substrate 12, and another epitaxial monocrystalline layer or film 14 of lead tin telluride or Pb_{1-x}Sn_xTe of the opposite conductivity type formed on the layer 12. The applications for this multilayer composite 13 include infrared detectors, as described subsequently.

It will be appreciated that where the IVA-VIA film(s) need not be monocrystalline, the substrate 12 may be amorphous, such as glass or fused quartz, or polycrystalline, such as polycrystalline aluminum oxide.

Referring now to FIG. 3, there is shown a schematic representation of a reactor system 20 which may be utilized to epitaxially form IVA-VIA compounds using the method of the present invention. The reactor typically comprises a quartz reactor chamber 21 containing an SiC-covered carbon pedestal 22 for supporting the substrate 12 (FIGS. 1 and 2) and an RF heating coil 23 which is connected to a power source (not shown). Although the dimensions are not critical, a chamber 21 about 6 cm in diameter by 40 cm in length has been used successfully. The temperature of the pedestal 22 and the substrate supported thereon may be measured by an infrared radiation thermometer (not shown) which may control the power to the coil 23. Means (not shown) may be provided for rotating the substrate, as shown by the arrow, to promote uniform deposition.

The reactant gases which form the IVA-VIA compounds enter the reactor chamber 21 via inlet line 24. Line 25 is used to exhaust the chamber of spent and unused reactants and gases, and to connect the chamber to sources of vacuum and air (not shown). The reactor system 20 uses stainless steel bubbler tanks such as tanks 31, 32 and 33 as needed for supplying the IVA-VIA film constituents, and bubbler tanks such as tank 34 for supplying conductivity-type determining impurities (n-type or p-type dopants). Alternatively, the dopants may be introduced in dilute form from a tank 35 containing the dopants and a carrier gas compatible with the growth process, e.g., H₂ or He, if such a dopant mixture is available.

Palladium-purified hydrogen is used as the carrier gas for the film constituents. The carrier gas is flowed from a source 37 through a liquid nitrogen cold trap 38 and through an assembly 39 of valve-controlled flow meters. The purified hydrogen then can be directed at a controlled rate through any or all of valves 41, 42, 43 and 44, respectively, (valves 81, 82, 83 and 84 being closed) into bubbler tanks 31, 32, 33 and/or 34, thereby transporting the desired reactant constituents in the bubblers through tank exit valves 46, 47, 48 and/or 49.

The constituents are then transported through valves 51, 52, 53 and/or 54 and, after proper mixing, through valve 62 to inlet line 24 and the reactor chamber 21. The spent reactant gases are exhausted from chamber 21 via lines 25 and valve 63.

Briefly, the process of forming composites 10 (FIG. 1) having layers or films 11 of IVA-VIA compounds or alloys comprises the steps of 1) evacuating the reactor chamber 21; 2) filling and flushing the reactor chamber with flowing hydrogen; 3) heating the pedestal 22 and pedestal-supported substrate 12 to the deposition temperature; 4) equilibrating the flow of gas from the bubbler tanks by connecting the appropriate tanks to exhaust (via valves 66, 67, 68, 69 and 72) and bubbling hydrogen therethrough at a controlled rate to equilibrate the flows at a predetermined ratio; 5) directing reactant gases into the reactor chamber to form the film of IVA-VIA compound or alloy; and 6) cooling the deposition composite to room temperature in hydrogen after diverting the reactant gases from the reactor. The formation of a layer of lead on the substrates prior to deposition per step 5 is an important part of the process for growing continuous, monocrystalline, lead-containing films 11, such as lead telluride and lead tin telluride, on insulative oxide substrates, such as magnesium aluminate and sapphire.

To evacuate the reactor according to step 1, valve 55 is opened to connect the reactor chamber 21 to vacuum. The flow lines up to the valves of the bubbler tanks 31, 32, 33 and/or 34 may also be connected to vacuum and evacuated through valves 56, 57, 58 and 59, respectively prior to filling with H₂.

According to step 2, the reactor chamber is purged by flowing hydrogen from tank 37 through flow meter valve 61 and inlet valve 78 to the inlet line 24 and the reactor chamber 21, then exhausting the hydrogen from the chamber through line 25 and exhaust valve 63.

The equilibration of gas flow (step 4) may be initiated simultaneously with the equilibration of the temperature of the pedestal 22 (step 3). That is, while the pedestal is being brought to deposition temperature, the hydrogen gas may be flowed through the bubbler tanks, as described previously, and diverted through valves 51, 52, 53 and 54 (valves 66, 67, 68 and 69 and common vacuum valve 70 are closed) to exhaust and equilibrate the flows through valves 75 and 72 at a predetermined ratio. The flows may be controlled using the valves associated with the flow meter assembly 39.

According to step 5, after the pedestal 22 and substrate 12 are at the deposition temperature and the flow rates have been equilibrated, valve 62 is opened, valve 75 is closed and the gas reactants are directed into the reactor chamber 21. It will be noted that the reactant gases are channeled into a single line, inlet line 24, prior to entering the reactor chamber. By channeling the reactant gases into the single inlet line 24, the gases, which are mixed externally to the heated reactor chamber can be introduced simultaneously into the reactor, thereby precluding an undesirable premature reaction of individual reactants with the heated substrate. Also, the valves 66-69 permit individual setting of the gas reactants prior to their mixing and introduction into the reactor chamber. Moreover, the valves 51-54 permit introduction of individual reactants prior to deposition per step 5 to promote the growth of films on materials such as sapphire and magnesium aluminate, as discussed previously.

After a predetermined deposition time involving step 6, the resulting composite is allowed to cool by shutting off power to the RF heating coil 23 after diverting the reactant gases from the reactor chamber 21 and through valves 66-69, 75 (with valve 62 closed), and 72. At the same time, hydrogen is still flowing through the reactor chamber via valves 61, 78, and 63, thereby cooling the sample in flowing carrier gas.

When the reactants and sources of dopant are normally gaseous at room temperature or are sufficiently volatile so that transport by a carrier gas may be considered optional, step 4 of the process can involve equilibrating the flows of these reactants or sources of dopants supplied by tank 35 with the other reactants by connection to the flow system via valve 71. If it is preferred that members of the reactant mixture meet in inlet line 24 of the reactor via separate lines, then the appropriate flows can be directed through valve 77 after adjusting the flows using flowmeter valve 76 and exhaust valve 73, which is closed immediately after valve 71 or 77 is opened. At the end of the deposition, the valve positions are reversed in order to remove (exclude) the reactant gases from the reactor.

FIG. 3 is used for purposes of illustration and instruction as to technique. Modifications in the design are within the capabilities of those skilled in the area of chemical vapor deposition.

SUBSTRATES

The Group II fluorides, particularly BaF_2 , are of considerable interest as substrates for IVA-VIA compounds because their thermal expansions approximate those of the IVA-VIA compounds, and because they are essentially transparent to 10-12 μm radiation in thin wafer form. BaF_2 considered an excellent substrate for IVA-VIA IR detectors at these wavelengths. Also, the insulative metallic oxides sapphire, magnesium oxide (MgO), and magnesium aluminate have properties which make them of interest as substrates for IVA-VIA compounds which can be used as detectors in the 3-5 μm range. For example, except for MgO , they are more stable than fluorides in the atmospheres used for the growth of the films.

BaF_2 and CaF_2 were used primarily in the form of cleaved (111)-oriented wafers made from crystal ingots, although some polished BaF_2 substrates of (111) orientation and (100) orientation which were prepared from (111) oriented crystal ingots were successfully used for monocrystalline film growth. The (111)-oriented BaF_2 and CaF_2 crystal ingots were typically about one inch in diameter and up to one inch in length and were used to form substrates of about 0.020 to 0.030 inch thickness.

In addition to the above, single crystal alkali halides, represented by NaCl , II-VI compounds, represented by CdTe , III-V compounds, represented by GaAs , and IV-VI compounds, represented by PbTe , were used as substrates for the epitaxial growth of the IV-VI compounds. The alkali halides were cleaved just prior to use; the CdTe was a single crystal film grown on a sapphire ($\alpha\text{-Al}_2\text{O}_3$) substrate; and the GaAs were (100) and (111)-oriented single crystal substrates, which were polished by chemical-mechanical means, and as-grown (111)-oriented films on sapphire. PbTe substrates (see Table II, composite type nos. 12 and 13) were polished by chemical-mechanical means and were oriented to expose a (100) plane.

In general it can be expected that the process can be used to produce IVA-VIA films on IVA-VIA substrates which possess similar lattice parameters. See, e.g., the above-mentioned article in *J. Crystal Growth* authored by one of the present inventors which is hereby incorporated by reference. The various metalorganic compounds used for IVA-VIA film growth are listed in Table I below.

TABLE I

METALORGANIC COMPOUNDS USED IN DEPOSITION OF IVA-VIA FILMS		
Compound	Abbreviation	Formulation
Tetramethyllead	TMFb	$(\text{CH}_3)_4\text{Pb}$
Tetraethyllead	TEPb	$(\text{C}_2\text{H}_5)_4\text{Pb}$
Tetramethyltin	TMSn	$(\text{CH}_3)_4\text{Sn}$
Tetraethyltin	TESn	$(\text{C}_2\text{H}_5)_4\text{Sn}$
Dimethyltellurium	DMTe	$(\text{CH}_3)_2\text{Te}$
Diethyltellurium	DETe	$(\text{C}_2\text{H}_5)_2\text{Te}$
Trimethylantimony	TMSb	$(\text{CH}_3)_3\text{Sb}$

Hydrogen telluride (H_2Te) is a suitable substitute for DMTe as a source of Te.

PbTe FILMS/SAPPHIRE AND MAGNESIUM ALUMINATE (SPINEL) SUBSTRATES

Here, tetraethyllead, TePb , and dimethyltellurium, DMTe, were used as the source of Pb and Te, respectively, in the stainless steel bubbler tanks 31 and 33. Polished, (0001)-oriented sapphire and polished, (111)-oriented magnesium aluminate were used as substrates 12 (FIG. 1).

After evacuating the reactor chamber 21 (step 1) and filling the reactor chamber with hydrogen flowing at approximately 10 liters per minute (1 lpm), (step 2), the pedestal 22 was heated by the RF coil 23 to within the desired deposition temperature range of approximately 450°-650° C. Hydrogen flow rates of approximately one lpm through the TEPb and 25-75 CCPM through the DMTe were used.

To promote rapid growth of continuous, monocrystalline PbTe films 11 (FIG. 1) on the sapphire and magnesium aluminate substrates 12, the substrate was nucleated with a thin deposit of lead prior to the onset of PbTe deposition. Typically, this was achieved within the preferred deposition temperature range of approximately 450°-650° prior to step 5 (or as an initial substep of step 5) by 1) introducing TEPb alone into the reactor chamber 21 to deposit Pb on the heated substrate, 2) next introducing DMTe alone into the reaction chamber, and 3) followed by the reintroduction of TEPb together with the DMTe into chamber 21, according to step 5.

More specifically, valves 51 and 62 were opened and valve 66, which had been open to exhaust the TEPb during flow equilibration (step 4), was closed, in order to direct TEPb alone into the reactor chamber 21. As mentioned previously, a hydrogen carrier gas flow rate of one lpm was used for the TEPb . After about one minute at this flow rate, sufficient Pb growth occurred to form a Pb deposit. Next valve 66 was opened to direct the TEPb to exhaust and valve 51 was closed. Valve 53 was then opened to introduce DMTe into the reactor through valve 62 with valve 68 closed. The DMTe converts Pb to PbTe and/or provides a tellurium rich atmosphere. A hydrogen flow rate through the DMTe of about 45 CCPM was used. After about five minutes of DMTe flow, TEPb was reintroduced into the reactor chamber in the carrier gas in the presence of DMTe (step 5) and PbTe was formed in the presence of the Te rich atmosphere.

TABLE II

CRYSTALLOGRAPHIC RELATIONSHIPS, IVA-VIA FILMS AND SUBSTRATES			
COMPOSITE TYPE NO.	SUBSTRATE PLANE	PARALLEL PLANES	PARALLEL DIRECTIONS
1	(0001) α -Al ₂ O ₃	(111) PbTe // (0001) Al ₂ O ₃	[110] PbTe // [1210] Al ₂ O ₃
2	(111) MgAl ₂ O ₄	(111) PbTe // (111) MgAl ₂ O ₄	[211] PbTe // [101] MgAl ₂ O ₄
3	(111) BaF ₂ (cleaved)	(111) PbTe // (111) BaF ₂	[110] PbTe // [011] BaF ₂
4	(100) NaCl	(100) PbTe // (100) NaCl	not determined
5	(100) MgO	(100) PbTe // (100) MgO	not determined
6	(0001) α -Al ₂ O ₃	(111) PbS // (0001) Al ₂ O ₃	[110] PbS // [1210] Al ₂ O ₃
7	(111) BaF ₂ (cleaved)	(111) PbS // (111) BaF ₂	[110] PbS // [011] BaF ₂
8	(111) CaF ₂	(111) PbS // (111) CaF ₂	[110] PbS // [011] CaF ₂
9	(0001) α -Al ₂ O ₃	(111) PbSe // (0001) Al ₂ O ₃	[110] PbSe // [1210] Al ₂ O ₃
10	(111) BaF ₂	(111) PbSe // (111) BaF ₂	[110] PbSe // [011] BaF ₂
11	(111) CaF ₂	(111) PbSe // (111) CaF ₂	[110] PbSe // [011] CaF ₂
12	(100) PbTe	(100) PbTe // (100) PbTe	not determined
13	(100) PbTe	(100) Pb _{0.8} Sn _{0.2} Te // (100) PbTe	not determined

After the film 12 of PbTe was deposited, the gas reactant mixture was diverted from the reactor chamber 21 and the sample was cooled in hydrogen flowing at about one 1pm (step 6).

The PbTe films were grown to about 5 μ m thickness on the sapphire and magnesium aluminate substrates. The films were determined to be monocrystalline using x-ray analysis. The crystallographic relationships between the PbTe films and alumina and spinel substrates are summarized in Table II, under composite type numbers 1 and 2. Growth parameters are summarized in Table III, also under composite type numbers 1 and 2.

PbTE FILMS/BaF₂ SUBSTRATES

PbTe films were grown on single crystal BaF₂ substrates using TEPb or TMPb and DMTe as the reactants. Some substrates were used as-cleaved, without polishing.

Monocrystalline film growth on the cleaved, (111)-oriented BaF₂ substrates was achieved using TEPb as the source of Pb at pedestal temperatures of 450°-600° C. Specifically, temperatures of 450, 500, 560, 575 and 600° C were utilized. Somewhat higher temperatures can also be expected to be consistent with single crystal growth. Also, the range of 500°-600° C provided a growth rate (0.08 μ m/min. or 5 μ m/hr. for the stated parameters) which was approximately twice that achieved at 450° C.

The PbTe films were grown to a thickness of approximately 5 microns. X-ray diffraction measurements showed the PbTe films were monocrystalline. The film-substrate crystallographic relations for PbTe films grown on the cleaved, (111)-oriented BaF₂ are indicated in Table II under composite type no. 3. The growth parameters described above are summarized in Table III under composite type no. 3A.

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TABLE III

GROWTH PARAMETERS FOR IVA-VIA FILMS

Sample Composite Type No.	1	2	3A	3B	3C	3D	3E	3F	3G	3H	3I	3J	3K	3L
Substrate	(0001) Al ₂ O ₃	(111) MgAl ₂ O ₄												
Film Deposition	500-600	450-600												
Carrier Gas Flow Rate (ccpm)			50	100	200	200								
TMPb	1000	1000					1000	750-2000	1000-3000	2000	2000	2000	2000	2000
TESe								75-150	75-150	75	75	75	75	75
DMTe	25-75	50	75	75	75	35	25	150	7	20	26	26	26	125
TMSb														
Flow Rate (ccpm)														
H ₂ S														
H ₂ Se														
Growth Rate (μm/hr)	~8	~8	~5	4.5	1.1	32	24	7-8	7-23	18	25	22	27	24
Film Thickness (μm)	~5	~5	~5	2.6	13.8	16.0	4.6	~	~15	8	25	11	13	18
Film Conductivity Type	—	—	p	p	p	n	p	—	p	p	n	n	n	n
Electrical Properties	—	—	—	0.1	0.0057	0.14	0.05	—	0.0014*	0.002	0.002	0.004	0.0006	0.0004
Resistivity (ohm-cm)	—	—	—	1.2×10 ¹⁷	1.8×10 ¹²	3.3×10 ¹⁶	2.0×10 ¹⁹	—	9.5×10 ¹⁸	6.9×10 ¹⁸	3.0×10 ¹⁹	1.5×10 ¹⁹	8.1×10 ¹⁸	2.5×10 ¹⁹
Carrier Concentration (cm ⁻³)	—	—	—	84	632	505	886	—	470 ⁺	440	101	933	904	620
Mobility (cm ² /V-sec.)	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sample Composite Type No.								4	5	6	7	8	9	10
Substrate								(100) NaCl	(100) MgO	(111) Al ₂ O ₃	(111) BaF ₂	(111) CaF ₂	(111) Al ₂ O ₃	(111) CaF ₂
Film Deposition								500-	550	550	550	550	550	550
Temp (°C)														
Carrier Gas Flow Rate (ccpm)														
TMPb								1000	1000	100	100	100	100	100
TEPb								25	25	—	—	—	—	—
TESe								—	—	—	—	—	—	—
DMTe								—	—	—	—	—	—	—
TMSb														
Flow Rate (ccpm)														
H ₂ S														
H ₂ Se														
Growth Rate (μm/hr)														
Film Thickness (μm)														
Film Conductivity Type														
Electrical Properties														
Resistivity (ohm-cm)														
Carrier Concentration (cm ⁻³)														
Mobility (cm ² /V-sec.)														

*Flow rates of 50,2000,75 cccpm through TMPb, TESe and DMTe, resp; temp. 625° C.

— indicates data not taken

Similar results were obtained using TMPb as the source of Pb , as shown below, except that growth rates could be increased considerably.

The metal organic CVD process of the present invention was used successfully to vary the conductivity type. That is, both n- and p-type PbTe films were formed on cleaved (111) BaF_2 substrates. Here, TMPb and DMTe were the sources of lead and tellurium. In these examples, the n-type and p-type films were obtained by varying the TMPb to DMTe ratio. See Table III, composite type no's. 3B-3E. For composite type no. 3D, hydrogen flow rates of 200 cccpm through the TMPb and 75 cccpm through the DMTe gave a TMPb:DMTe flow rate ratio of about 3:1, and provided a high film growth rate of about 32 microns per hour and a very high quality, monocrystalline n-type (presumably metal rich) PbTe film. However, for high TMPb concentrations and low DMTe concentrations, p-type films were formed, perhaps due to a high defect structure. Thus, composite type no. 3E was p-type, when the DMTe flow was lowered from 75 to 35 cccpm. Varying the ratios of TEPb and DMTe can thus be expected to yield n- and p-type films with controllable properties.

N-type on p-type and p-type on n-type multilayer 25 films and junctions were formed by varying the ratios of the Group IVA and VIA reactants.

PbTe FILMS/NaCl SUBSTRATES

The method and metalorganic constituents used for 30 the formation of PbTe films on BaF_2 substrates were used to form monocrystalline PbTe films on (100)-oriented NaCl substrates. Here, deposition was attempted and achieved at temperatures in the range of 500°-625° C. The crystallographic relationships of the PbTe films 35 and NaCl substrates are listed in Table II under composite type no. 4. Growth parameters are listed in Table III, also under composite type no. 4, for samples grown within the approximate range 500°-550° C. This range produced better quality films on NaCl than higher temperatures. The NaCl substrates appeared to be unstable at higher temperatures.

PbTe FILMS/MgO SUBSTRATES

The method and metalorganic constituents used for 45 the formation of PbTe/BaF_2 and PbTe/NaCl composites were also used to form monocrystalline PbTe films on MgO substrates. The crystallographic relationships and growth parameters are listed in Table II and III under composite type no. 5. As was true for PbTe/NaCl 50 composites, better quality films were produced within the range 500°-550° C than at higher temperatures.

Similar results can be expected when TMPb is used as a substitute for TEPb .

PbTe FILMS/GaAs, GaAs-on- Al_2O_3 , and CdTe-on- Al_2O_3 SUBSTRATES

The method and metalorganic constituents used for the formation of PbTe films on BaF_2 and NaCl substrates were used to form epitaxial PbTe films on polished (100) and (111)-oriented GaAs substrates, on (111) GaAs films grown on (0001) Al_2O_3 ; and on (111) CdTe films grown on (1126) Al_2O_3 . Typical flow rates of 50-200 cccpm for TMPb and 75-100 cccpm for DMTe were used at growth temperatures of 500 and 625° C to form films which were very highly ordered with respect to the underlying substrate. Because lead telluride (PbTe) is representative of lead tin telluride ($\text{Pb}_{1-x}\text{Sn}_x\text{Te}$), lead tin telluride can be grown on sub-

strates which are suitable for PbTe growth. Thus, using similar conditions and, of course, a source of tin, such as TESn , lead tin telluride can be grown on the above-described substrates.

PbS AND PbSe FILMS

The method of the present invention was also used to form monocrystalline, continuous films of PbS and PbSe on polished (0001) Al_2O_3 , cleaved (111) BaF_2 , and cleaved (111) CaF_2 substrates using a 550° C deposition temperature. The Group VIA source was H_2S and H_2Se . The crystallographic relationships for the $\text{PbS/(0001)Al}_2\text{O}_3$, PbS/(111)BaF_2 , $\text{PbSe/(0001)Al}_2\text{O}_3$, PbSe/(111)BaF_2 and PbSe/(111)CaF_2 film-substrate composites are listed in Table II, under composite type no's. 6-11, respectively. The growth parameters are listed in Table III under composite type no's 6-11.

Referring to Table III, the PbS films for composite types 6-8, and the PbSe films for composite types 9-11 were formed from TMPb and, respectively, H_2S and H_2Se . The H_2S and H_2Se were supplied from tank 35, which is connected to the reactor system through valves 76 and 77 or 76, 71 and 62. Valve 73 or 75 is used to equilibrate the flows from tank 35 prior to introduction into line 24 and reactor 21. Valve 75 is also used in mixing the H_2S or H_2Se (a carrier gas is optional) from tank 35 with the carrier gas transported reactants from the bubbler tanks prior to entry into the reactor chamber 21 (step 5).

When the substrate is stable to the Group VIA reactants at the growth temperature and the product of decomposition does not form a deposit on or react with the substrate surface, the Group VIA reactant can be introduced into the reactor prior to the introduction of the Group IVA reactants. For example, reaction of BaF_2 with DMTe precluded introducing DMTe into the reactor prior to the introduction of TEPb or TMPb and mixing of the reactant gases external to the reactor was, therefore, required. In the case of the Group VIA hydrides, namely H_2S and H_2Se , which did not appear to react with BaF_2 , it was sufficient to introduce the VIA containing reactants either singly or together into the reactor prior to the introduction of the metallorganic Pb and/or Sn compounds. Referring to FIG. 3, in the latter case, the Group VIA component would pass through valve 77 into reactor 21 prior to the admittance of the Group IVA component(s) through valve 62.

It will be appreciated by those skilled in the art that pyrolysis of mixtures of the hydrides of S and Se with the Group IVA components will form Group IVA- $\text{S}_{1-x}\text{Se}_x$ compounds such as $\text{PbS}_{1-x}\text{Se}_x$ or $\text{SnS}_{1-x}\text{Se}_x$.

$\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ FILMS/ BaF_2 SUBSTRATES

Lead tin telluride films were grown on cleaved, (111)-oriented BaF_2 substrates at deposition temperatures of 550°-625° C using essentially the lead telluride-on-barium fluoride deposition method with the added film constituent—tin—being supplied by TESn from stainless steel bubbler tank 32. Film growth of composition $x = 0$ to $x = 0.2$ was achieved for hydrogen flow rates through the TESn of up to 2000 cccpm. (As the hydrogen flow rate through the TESn is decreased to zero, the film composition approaches that of lead telluride). Using a hydrogen flow rate of 25 cccpm through the DMTe and 1000 cccpm through the TEPb , the desired composition for detector devices, $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ or $x = 0.2$, was closely approximated over a wide range of

hydrogen flow rates (approximately 750-2000 cccpm) through the TESn. Precisely the desired composition was achieved for hydrogen flow rates through the TESn of 850 and 900 cccpm. Growth rates using the temperature range 550°-625° C and the range of hydrogen flow rates of 750-2000 cccpm were approximately 7 to 8 microns per hour. See Table III, composite type No. 3F.

Lead tin telluride films were also grown using TMSn in place of TESn. However, the TMSn was considerably less efficient than TESn for the deposition temperature used, 550°-600° C.

Referring to Table III, composite type No. 3G, growth rates of about 7-23 $\mu\text{m}/\text{hr}$. were obtained over the temperature range 550°-625° C using TMPb in place of TEPb, for a DMTe flow rate of 75-150 cccpm, a TESn flow rate of 3000 cccpm, and a TMPb flow rate of approximately 50 cccpm. Growth rates increased with temperatures in the range 550°-625° C. However, at the higher temperatures, the value of x increased. To control the film composition to $x = 0.2$ at 625° C it was necessary to use a TESn flow rate of about 2000 cccpm, indicated below.

For hydrogen flow rates through the respective reactants TMPb, TESn and DMTe of 50, 2000 and 75 cccpm and a pedestal temperature of 625° C, a film of composition $\text{Pb}_{0.50}\text{Sn}_{0.20}\text{Te}$ was grown to a thickness of approximately 15 micron at a growth rate of about 23 micron per hour on (111) BaF_2 substrates. The film possessed excellent electrical properties at room temperatures: resistivity was approximately 0.0014 ohm-cm; hole concentration was $9.5 \times 10^{18} \text{ cm}^{-3}$; mobility was about 470 $\text{cm}^2/\text{V}\cdot\text{sec}$; and the band-gap energy was about 0.23 eV.

Sawed and polished (111) BaF_2 wafers were also used as substrates. The appearance of lead tin telluride films grown on polished BaF_2 substrates was inferior to those grown on freshly cleaved BaF_2 , but the electrical properties were essentially the same.

Using the foregoing information, those skilled in the art will achieve film compositions within the range $0 \leq x \leq 0.5$.

VARIED CONDUCTIVITY-TYPE $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ FILMS

The conductivity type of lead tin telluride films was changed by varying the DMTe flow rate and growth temperature. As shown by the data in Table III, alkyl antimony compounds such as TMSb can also be used as a source of n-type doping impurity to vary the conductivity type of lead tin telluride. Referring to FIG. 3, TMSb was stored at -78° C in the stainless steel bubbler tank 34. Hydrogen was used to transport the TMSb for mixing with the other reactants externally to the reactor chamber 21.

As shown by composite nos. 3H-3L in Table III, increasing the TMSb flow rate changes the film from p-type to n-type. The TMSb flow rate at which this type change occurs is dependent upon the other parameters, such as TMPb, TESn and DMTe flow rates and film growth temperature. Table III indicates the film composition can be closely controlled and that electrical properties for the p-type and n-type films are generally excellent.

Considerable tensile stress was present in PbTe and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ films grown on BaF_2 substrates, mainly because of the large difference between the thermal expansion coefficients of the film materials and the BaF_2 substrate material. To illustrate, BaF_2 and PbTe

have coefficients of approximately $18 \times 10^{-6}/^\circ\text{C}$ and $27 \times 10^{-6}/^\circ\text{C}$, respectively. However, despite the existence of stress, $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ films 100 microns thick were grown on BaF_2 substrates without evidence of cracking. Such composites may be useful as strain gauges, etc.

DOUBLE LAYER $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ FILMS/ BaF_2 SUBSTRATES

Referring now to FIG. 2 using a cleaved, (111)-oriented BaF_2 substrate 12, a first, undoped p-type layer 11 of $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ was epitaxially formed on the substrate, then a second $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ layer 14 doped with Sb was grown on the first layer. Both layers were formed using the method of the present invention, as described previously. The double layer, $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ film- BaF_2 substrate composite 13 was processed into a mesa diode (not shown) by standard photolithographic techniques. Ohmic contact was provided by vacuum deposition of a one micron thick film of Sn on the surface of the upper layer 14. An infrared photovoltaic effect of about 25 mv was observed at 77° K.

Sn-VIA FILMS

The reaction of TESn with DMTe, H_2S and H_2Se was used to form Sn-VIA compound films. For each film, the new H_2 flow through the TESn was kept constant at 2000 cccpm. The flow through DMTe and the H_2S and H_2Se flows were arbitrarily set at 75 cccpm, ~25 cccpm, and ~50 cccpm, respectively.

Within the temperature range ~500°-650° C, ordered growth of SnTe was obtained on the substrates examined, cleaved (111) BaF_2 and polished (100) PbTe . Considerable trigonal structure usually associated with (111) growth was obtained on the BaF_2 , particularly near the edges of the substrate. Growth on (100) PbTe produced a large array of islands oriented with respect to each other and the substrate. Large crystallites with parallel faces and, in some cases prominent hollow centers grew at the edges of the PbTe substrates under these less-than-optimum growth conditions.

S and Se chalcogenides of tin were grown over the deposition temperature range of ~500°-575° C. Above 575° C, e.g. at 600° C, film quality decreased. The VIA constituents S and Se were provided by H_2S and H_2Se , respectively, using arbitrarily-chosen flow rates of ~25 and ~50 cccpm, respectively.

The nature of the growth of the S and Se chalcogenides of Sn, which possess an orthorhombic structure, was not like that of cubic SnTe. Tinsulfide films, ~3 μm thick, grown at 550° C simultaneously on cleaved BaF_2 and CaF_2 tended to peel from the BaF_2 but adhered to the CaF_2 . At 500° C tin selenide grew as crystallites on BaF_2 . An orienting influence of the substrate was suggested by the parallelism and 60 degree symmetry displayed by many of the crystallites. In the early growth stages the films possessed a yellow-orange color; thicker films were grey. Crystallite growth of both compounds was obtained on (0001) Al_2O_3 .

Continuous film growth of the tin-VIA compounds on sapphire can be expected if the surface is nucleated with Sn prior to the growth of the tin-VIA compounds, as previously described for PbTe growth on sapphire and magnesium aluminate.

Thus, there has been described a method of growing VIA-VIA films on insulative and semiconducting substrates. Examples of the method of growth, of the film-substrate composites formed thereby, and of applica-

tions for the composites have been described. However, the scope of the invention is limited only by the appended claims.

Having thus described a preferred embodiment, what is claimed is:

1. A method for forming a layer of Group IVA-VIA material on an amorphous substrate of glass or fused quartz or a monocrystalline or a polycrystalline substrate selected from the group consisting of Group IA - Group VIA compounds, Group II - Group VI compounds Group IIA - Fluorides, Group IIIA - Group VA compounds and Group IV - Group VI compounds, α -Al₂O₃ and MgAl₂O₄, comprising the steps of:

establishing a heated deposition zone at a temperature within the range 400°-700° C and encompassing a deposition surface of said substrate; forming a gaseous mixture of metalorganic IVA-containing and VIA-containing components; and pyrolyzing said mixture within said heated deposition zone.

2. A method for forming a layer of Group IVA-VIA material on a substrate as defined in claim 1 wherein: the layer of IVA-VIA material is a monocrystalline layer of PbS or PbSe;

the Group VIA containing component is selected from H₂S or H₂Se; and the Group VIA-containing component is introduced into the heated deposition zone prior to introduction of the Group IVA-containing component.

3. A method for forming a layer of Group IVA-VIA material on a substrate as defined in claim 1, wherein the substrate is a monocrystalline Group IA-VIIA material.

4. A method for forming a layer of Group IVA-VIA material on a substrate as defined in claim 1, wherein the substrate is a monocrystalline Group IIA-fluoride material.

5. A method for forming a layer of Group IVA-VIA semiconductor on a substrate as defined in claim 1, wherein the substrate and layer are monocrystalline, the group IVA-VIA material is selected from lead telluride and lead tin telluride, and the substrate is selected from α -Al₂O₃ and magnesium aluminate, the method further comprising the step of forming a layer of Pb on the deposition surface of the substrate prior to the formation of lead telluride or lead tin telluride.

6. The method for forming a layer of Group IVA-VIA semiconductor material on a substrate as defined in claim 1, wherein the Group IVA-VIA material is a tin-VIA material and the substrate is selected from α -Al₂O₃ and magnesium aluminate the method further comprising the step of forming a layer of tin on the deposition surface of the substrate prior to the formation of the tin-VIA material.

7. The method defined in claim 6 wherein the VIA constituent of the tin-VIA material is at least one element selected from the group consisting of sulfide, selenide and telluride.

8. A method for epitaxially forming at least one monocrystalline layer of IVA-VIA semiconductor material on a deposition surface of a monocrystalline substrate selected from the group consisting of Group IA - Group VIA compounds Group II - Group VI compounds, Group IIA - Fluorides, Group IIIA - Group VA compounds and Group IV - Group VI compounds, α -Al₂O₃ and MgAl₂O₄, said IVA constituent being selected from Pb and Sn and said via constituent being selected from S, Se and Te, the method comprising the step of:

establishing a heated, deposition zone at a temperature within the range 450° - 650° C and encompassing the deposition surface of the substrate;

forming a gaseous mixture of IVA-containing compounds selected from the group consisting of tetraethyllead, tetramethyllead, tetramethyltin, tetraethyltin, and of VIA-containing compounds selected from the group consisting of dimethyltellurium, H₂Te, diethyltellurium, hydrogen sulfide, and hydrogen selenide; and

pyrolyzing said gaseous mixture within said deposition zone.

9. A method for epitaxially forming at least one monocrystalline layer of IVA-VIA semiconductor material on a deposition surface of a monocrystalline substrate as defined in claim 8, wherein the VIA-containing compound is hydrogen sulfide or hydrogen selenide and is introduced into the deposition zone prior to the introduction of the IVA-containing compound.

10. The method defined in claim 8, further comprising the steps of;

varying the ratio of said IVA-containing and VIA-containing compounds in said mixture to form layers of different compositions; and selectively introducing conductivity-type determining impurities into said gaseous mixture.

11. The method defined in claim 10 wherein the conductivity-type determining impurity is Sb and is supplied by a metalorganic alkyl compound of Sb.

12. The method defined in claim 10 wherein the monocrystalline substrate is selected from the group consisting of Group IA-VIIA, Group IIA-fluoride, Group IIIA-VA, and Group IIB-VIA materials.

13. The method recited in claim 1 wherein said substrate is monocrystalline.

14. The method recited in claim 1 wherein said substrate is polycrystalline.

15. The method recited in claim 1 wherein said substrate is amorphous.

* * * *



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	:	Sven Lindfors et al.)	Group Art Unit 1765
Appl. No.	:	09/835,931)	
Filed	:	April 16, 2001)	
For	:	METHOD OF GROWING A THIN FILM ONTO A SUBSTRATE)	
Examiner	:	Kunemund, Robert M.)	

ON APPEAL TO THE BOARD OF PATENT APPEALS AND INTERFERENCES

APPLICANT'S BRIEF



Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Applicant, in the above-captioned patent application, appeals the final rejection of Claims 1-33. This appeal is proper under 35 U.S.C. §134 and 37 C.F.R. § 191(a).

This appeal brief is filed in triplicate. A check in the amount of \$330 is included to cover the fee for filing the appeal brief pursuant to 37 C.F.R. § 1.17(c). Please charge any additional fees which may be required to Deposit Account No. 11-1410.

I. STATEMENT OF INTEREST

Pursuant to 37 C.F.R. § 1.192(c)(1), Applicant hereby notifies the Board of Patent Appeals and Interferences that ASM International N.V., a Netherlands corporation with its principle place of business at Jan van Eycklaan 10 3723 BC Bilthoven, THE NETHERLANDS, has acquired the

entire right, title and interest to the above-captioned patent application by virtue of an assignment from ASM Microchemistry OY, a Finnish corporation having offices at Kutojantie 2B, 02630 Espoo, Finland. A copy of this assignment executed on November 26, 2003 and recorded on December 17, 2003 is provided in the Appendix B. ASM Microchemistry OY obtained the entire right, title and interest to the above-captioned patent application by virtue of an assignment from the inventors. That assignment is recorded in the U.S. Patent and Trademark Office at Reel/Frame 012029/0763.

II. RELATED APPEALS AND INTERFERENCES

Pursuant to 37 C.F.R. § 1.192(c)(2), Applicant hereby notifies the Board of Patent Appeals and Interferences that Applicant, Applicant's legal representative, and ASM International N.V., are unaware of any appeals or interferences that will directly affect, or will be directly affected by, or have any bearing on the Board's decision in the pending appeal.

III. STATUS OF THE CLAIMS AND AMENDMENTS

Claims 1-33 are pending.

Claims 34-67 have been canceled in an amendment filed in a separate paper.

Claims 1-33 stand rejected under 35 U.S.C. § 103(a) upon the grounds set forth in the Final Office Action.

Claims 1-33 are the subject of this appeal.

In accordance with 37 C.F.R. § 1.192(c)(9), a copy of the claims involved in the appeal are contained in the Appendix (Appendix A) attached hereto.

IV. SUMMARY OF THE INVENTION

In the atomic layer deposition (ALD) technique, one or two or more different reactants are sequentially and/or alternatingly supplied to a reaction chamber in a pulse-wise manner. The reactants are supplied to the reaction chamber in the vapor state or in the gaseous state.

Furthermore, the reactants used in ALD are typically mutually very reactive, even at room temperature. Therefore two or more reactants or subsequent pulses of the same reactant used in ALD should be kept well separated and supplied to the reactor strictly sequentially.

Accordingly, an embodiment of the present invention relates to a method for growing thin films onto a surface of a substrate by exposing the substrate to alternately repeated surface reactions of vapor-phase reactants. The method comprises providing a first reactant source and providing an inactive gas source. A first reactant is fed from the first reactant source in the form of repeated pulses to a reaction chamber via a first conduit. The first reactant is allowed to react with the surface of the substrate in the reaction chamber. Inactive gas is fed from the inactive gas source into the first conduit via a second conduit that is connected to the first conduit at a first connection point so as to create a gas phase barrier between the repeated pulses of the first reactant entering the reaction chamber. The inactive gas is withdrawn from the first conduit via a third conduit connected to the first conduit at a second connection point.

This embodiment provides a novel method for forming a gas phase barrier between repeated pulses of the first reactant. Specifically, through switching of an inert gas flow, the reactant vapor flow is alternatingly: (i) directed to the reaction chamber by an inert gas flow from the source container towards the reaction chamber and then (ii) prevented from flowing from the source container to the reaction chamber by an inert gas flow in a reverse direction in a part of the conduit connecting the source container and the reaction chamber. For embodiments that utilize more than one reactant, this embodiment also provides a gas phase barrier between pulses of a first reactant and a second reactant. In such embodiments, strict separation of two mutually reactive reactants, as required in ALD, can be achieved in a reliable way. One advantage of these method is that the switching valves may be configured such that they are only exposed to inert gas and not

to aggressive reactants that could corrode the valves. Furthermore, the valves can be installed outside the reactor's hot zone without a risk of condensing low vapor pressure reactant.

With reference to a specific embodiment of the invention, which is described in the Specification at page 14, line 9 to page 15, line 26 and illustrated in Figure 2, a first reactant source 24 and an inactive gas source 29 are provided. Page 14, lines 14-17. A first reactant is fed from the first reactant source 34 in the form of repeated pulses to a reaction chamber 27 via a first conduit 34. Page 14, line 18 to Page 15, line 13. The first reactant is allowed to react with the surface of the substrate in the reaction chamber 27. *Id.* Inactive gas is fed from the inactive gas source 21 into the first conduit 34 via a second conduit that is connected to the first conduit at a first connection point so as to create a gas phase barrier (See Figure 2 in Appendix B) between the repeated alternating pulses of the first reactant entering the reaction chamber 27. *Id.* The inactive gas is withdrawn from said first conduit via a third conduit 33 connected to the first conduit 34 at a second connection point. *Id.*

In another embodiment, which is described in the Specification at page 11, line 23 to page 13, line 20 and illustrated in Figure 1, the first reactant pulses that are separated from one another may be alternated with similar pulses of a second reactant.

V. ISSUE PRESENTED ON APPEAL

The following issue is presented: Whether the combination of Leskela et al. (M. Leskela et. al., "Synthesis of oxide thin films and overlayers by atomic layer epitaxy for advanced applications," Materials Science and Engineering Vol. B41 (1996), pages 23-29) in view of Manasevit et al. (U.S. Patent No. 4,066,481) was properly used to reject Claims 1-33 under 35 U.S.C. § 103.

VI. GROUPING OF THE CLAIMS

For the purposes of this appeal only, all of the appealed claims stand or fall together so as to simplify and narrow the issues on appeal. While the patentability of each claim will not be discussed individually, each claim does present distinct issues of patentability and Applicant respectfully reserves the right to separately argue in future continuing applications.

Group 1: Claims 1-33

VII. DISCUSSION OF THE REFERENCES RELIED UPON BY THE EXAMINER

In rejecting the claims, the Examiner relied upon the following references:

Leskela et al. (M. Leskela et. al., "Synthesis of oxide thin films and overlayers by atomic layer epitaxy for advanced applications," Materials Science and Engineering Vol. B41 (1996), pages 23-29) (Appendix C)

Leskela et al. provides an overview of atomic layer deposition ("ALD") chemistry. Leskela et al. is divided into five sections. In the first section (i.e., the Introduction), Leskela et al. provided an overview of the alternately pulsed reaction sequence that is common in ALD. In this sequence, "[g]aseous precursors are introduced one at a time to the substrate surface and between pulses the reactor is purged with an inert gas or evacuated. In the first reaction step, the precursor is saturatively chemisorbed at the substrate surface and during subsequent purging the excess precursor is removed from the reactor. In the second step the other precursor is introduced on the

substrate and the desired film growth takes place. After that the reaction byproducts and the precursor excess are purged out from the reactor.” Page 837. In the second section, Leskela et al. described the basic requirements of ALD precursors, which include volatility and sufficient vapor pressure. See pages 837-838. In the third section, Leskela et al. described precursor combinations and the surface as a reactant. In the fourth section, Leskela et al. described the chemistry of several non-metal and metal precursors. In the final section, Leskela et al. outlined future challenges in ALD, which included ALD precursor development.

Thus, Leskela et al. is relied upon for teaching standard ALD sequences including inert gas purges steps between reactant pulses.

Manasevit et al.(U.S. Patent No. 4,066,481) (Appendix D)

With reference to Figure 3, Manasevit et al. disclosed a reactor system 20, which may be used to epitaxially form a multilayer composite 13. Col. 3, lines 29-30. The system 20 includes a reactor chamber 21. The reactant gases enter the reactor chamber 21 via an inlet line 24. Col. 3, lines 46-46. The system 20 uses bubbler tanks 31, 32, 33 to supply reactants to the reactor chamber 21. Col. 3, lines 49-50. The carrier gas flows from a source 37 through a liquid nitrogen cold trap 38 and through an assembly 39 of valve-controlled flow meters. Col. 3, lines 59-63. The carrier gas can then be directed at a controlled rate through any or all of a series of valves 41, 42, 43, 44, respectively, (with a second series of valves 81, 82, 83 and 84 being closed) into the bubbler tanks 31, 32, 33, 34 thereby transporting the desired reactant constituents in the bubblers through a series of tank exit valves 46, 47, 48, 49. Col. 3, lines 63-68. The constituents are then transported through another series of valves 51, 52, 53, 54 and, after proper mixing, through a final valve 62 to the inlet line 24 and the reactor chamber 21. Col. 4, lines 1-5. The spent reactant gases are exhausted from the chamber 21 via an exhaust line 25 and an exhaust valve 63. *Id.*

Manasevit et al. described a method of using the system 20 as including: "1) evacuating the reactor chamber 21; 2) filling and flushing the reactor chamber with flowing hydrogen; 3) heating the pedestal 22 and pedestal-supported substrate 12 to the deposition temperature; 4) equilibrating the flow of gas from the bubbler tanks by connecting the appropriate tanks to exhaust (via valves 66, 67, 68, 69 and 72) and bubbling hydrogen therethrough at a controlled rate to equilibrate the flows at a predetermined ratio; 5) directing reactant gases into the reactor chamber to form the film of IVA-VIA compound or alloy; and 6) cooling the deposition composite to room temperature with hydrogen after diverting the reactant gases from the reactor." Col. 4, lines 8-20.

In step 4, equilibrating the flow of gas from the bubbler tanks, involves diverting the hydrogen gas through valves 51, 52, 53 and 54 to exhaust (while valves 66, 67, 68 and 69 and common vacuum valve 70 are closed) and equilibrate the flows through the exhaust valves 75, 72 at a predetermined ratio. Col. 4, lines 39-49 In step 5, reactant gases are directed to the reaction chamber, by opening valve 62 and closing the exhaust valve 75. Col. 4, lines 50-65. In this manner, the reactant gases are channeled into a single line, inlet line 24, prior to entering the reactor chamber. *Id.* By channeling the reactant gases into the single inlet line 24, the gases, which are mixed externally to the heated reactor chamber, can be introduced simultaneously into the reactor, thereby precluding an undesirable premature reaction of individual reactants with the heated substrate. *Id.* In step 6, the reactant gases are diverted from the reactor chamber 21 by closing valve 62 and opening the exhaust valve 75. *Id.*

Thus, Manasevit et al. merely discloses maintenance of a reactant flow while alternately diverting that flow through the reaction chamber and directly to exhaust.

VIII. ARGUMENT

A. The Combination Does Not Render Obvious the Method of Growing Thin Films onto a Surface of a Substrate as recited in Claims 1-33.

Claims 1-33 stand rejected under 35 U.S.C. § 103. The rejection of all of these Claims relies on the combination of Leskela et al. and Manasevit et al. However, this combination of references does not establish *prima facie* obviousness for the reasons set forth below.

Claim 1 recites method for growing thin films onto a surface of a substrate by exposing the substrate to alternately repeated surface reactions of vapor-phase reactants. The method comprises providing a first reactant source and providing an inactive gas source. A first reactant is fed from the first reactant source in the form of repeated alternating pulses to a reaction chamber via a first conduit. The first reactant is allowed to react with the surface of the substrate in the reaction chamber. Inactive gas is fed from the inactive gas source into the first conduit via a second conduit that is connected to the first conduit at a first connection point so as to create a gas phase barrier between the repeated alternating pulses of the first reactant entering the reaction chamber. The inactive gas is withdrawn from said first conduit via a third conduit connected to the first conduit at a second connection point.

The combination of Leskela et al. and Manasevit et al. does not set forth a *prima facie* case of obviousness. A *prima facie* case of obviousness requires that “all the claim limitations must be taught or suggested by the prior art.” *M.P.E.P. 2143.03*.

With respect to Leskela, this reference merely taught that in an ALD reactor “[g]aseous precursors are introduced one at a time to the substrate surface and between pulses the reactor is purged with an inert gas or evacuated.”

With respect to the Manasevit et al., this reference merely taught a reactor system that includes a reactor, a plurality of reactant sources, and a multitude of interconnected conduits and

valves for supplying the reactant to the reactor. *Importantly*, in the disclosed method for operating this reactor system, the valve 62 is opened and closed to permit or prevent the flow of the reactant to the reactor 21. *See* Col. 4, lines 50-54 and Col. 5, lines 4-8.

As such, Leskela et al. and Manasevit et al. do not teach or suggest, either alone or in combination, a method in which inactive gas is fed from the inactive gas source into the first conduit via a second conduit that is connected to the first conduit (which provides reactant) at a first connection point so as to create a gas phase barrier between the repeated alternating pulses of the first reactant entering the reaction chamber. The applied references also do not teach or suggest, either alone or in combination a method in which inactive gas is withdrawn from said first conduit via a third conduit connected to the first conduit at a second connection point. The Examiner has also not identified any suggestion in the references themselves or in the knowledge generally available to one of ordinary skill in the art to modify the references to include these operational steps. Thus, the Examiner has not set forth a *prima facie* case of obviousness.

In the Office Action dated September 11, 2002, the Examiner stated that it “would have been obvious to one of ordinary skill in the art to modify the Leskela et al reference by the teachings of the Manasevit et al reference to use the gases feed system of Manasevit et al. in order to obtain more uniform flows as set forth in the prior art.” However, as pointed out above, such a combination does not teach or suggest all of the claim limitations of Claim 1.

In response to Applicant arguments, in the final office action, the Examiner stated:

The Manasevit reference teaches the separate [and] controllable inert gas line which clearly meets the apparatus limitations of the inert gas supply line as claimed. Applicants are arguing the operational differences between the claims and the prior art. However, the instant claims are drawn to an apparatus only, and thus the prior art must merely meet the apparatus limitations and be capable of the use. In the instant case the combination of Manasevit and Leskala et al teach the claimed apparatus deposition system and due to the valves and bypasses in the references, the combined apparatus is clearly capable of being operated as shown in the specification.”

(emphasis added)

However, Claims 1-33 are method claims, which recite a number of specific operational steps as referenced above. Without admissions, Applicant submits that even if the combination had the capability to meet the claimed invention, the rejection of Claims 1-33 cannot be properly maintained by showing that the prior art “merely meet[s] the apparatus limitations and [is] capable of the use. Instead, to establish a *prima facie* case of obviousness, the Examiner must show that all of the operational steps of Claims 1-33 are taught or suggested by Leskela et al and Manasevit et al. See MPEP 2143.03. Applicants respectfully submit that the Examiner has not met this burden and cannot meet this burden by merely stating that the prior art “meets the apparatus limitations and is capable of the use.”

IX. CONCLUSION

Nothing in the prior art discloses, teaches or suggests the invention recited by the claims discussed above. In combination, the applied references also do not also art disclose, teach or suggest the invention recited by the claims discussed above. In addition, the art of fails to supply any motivation or suggestion to modify the applied references to include the limitations of the claims. The applied combinations of references therefore is improper.

The applied reference thus do not make the invention obvious. The final rejection of Claims 1-33 based on obviousness should be reversed. Favorable action to this end therefore is most respectfully solicited.

Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR

Dated: 1-6-09

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APPENDIX A

1. **(Previously presented)** A method for growing thin films onto a surface of a substrate by exposing the substrate to alternatively repeated surface reactions of vapor-phase reactants, the method comprising the steps of:

providing a first reactant source;

providing an inactive gas source;

feeding a first reactant from the first reactant source in the form of repeated alternating pulses to a reaction chamber via a first conduit;

allowing the first reactant to react with the surface of the substrate in the reaction chamber;

feeding inactive gas from the inactive gas source into the first conduit via a second conduit that is connected to the first conduit at a first connection point so as to create a gas phase barrier between the repeated alternating pulses of the first reactant entering the reaction chamber; and

withdrawing the inactive gas from said first conduit via a third conduit connected to the first conduit at a second connection point.

2. **(Original)** The method of Claim 1, further comprising the step of providing the second connection point upstream of the first connection point so that, at least for some length of the first conduit, the inactive gas fed into the first conduit flows upstream towards the first reactant source.

3. **(Original)** The method according to Claim 1, wherein the step of providing a first reactant source comprises vaporizing the first reactant.

4. **(Original)** The method according to Claim 3, wherein the step of providing a first reactant source further comprising maintaining the first reactant source at least at a vaporizing temperature of the first reactant.

5. **(Original)** The method of Claim 1, wherein the step of providing a first reactant source comprises freeing solid reactant from solid particles located within the first reactant source.

6. **(Original)** The method of Claim 1, wherein the step of providing a first reactant source comprises freeing liquid reactant from a suspended liquid in the first reactant source.

7. **(Original)** The method of Claim 1, further comprising the steps of providing a purifier and passing the first reactant through the purifier before transferring the first reactant into the reaction chamber.

8. **(Original)** The method of Claim 7, wherein the purifier is a filter comprising at least one of a ceramic molecular sieve and an electrostatic filter capable of separating one of at least dispersed liquid, solid droplets, particles and molecules of a minimum molecular size from the reactant gas flow.

9. **(Original)** The method according to Claim 7, wherein the purifier is an active purifier comprising functional groups capable of reacting with components present in the reactant gas flow.

10. **(Original)** The method of Claim 7, wherein the step of providing a purifier further includes providing the purifier along the first conduit between the second connection point and the first reactant source.

11. **(Original)** The method of Claim 10, further including only passing the first reactant over the purifier in a signal direction.

12. **(Original)** The method according to Claims 10, further comprising the step of forming the gas phase barrier between the purifier and the reaction chamber.

13. **(Original)** The method according to Claim 1, further comprising providing the second connection point between the first connection point and the first reactant source.

14. **(Original)** The method of Claim 1, further comprising the step of maintaining the third conduit at a temperature at least equal to a condensation temperature of the first reactant.

15. **(Original)** The method according to Claim 1, further comprising the step of maintaining the second conduit at a temperature no greater than a reaction temperature of the reaction chamber.

16. **(Original)** The method according to Claim 1, wherein the third conduit is an open gas flow channel.

17. **(Original)** The method according to Claim 1, wherein the third conduit does not include valves.

18. **(Original)** The method according to Claim 1, wherein the first conduit does not include valves.

19. **(Original)** The method according to Claim 1, further comprising the steps of providing an outlet conduit for withdrawing unreacted reactants from the reaction chamber and connecting the third conduit to the outlet conduit.

20. **(Original)** The method according to Claim 1, further comprising the steps of providing an outlet conduit for withdrawing unreacted reactants from the reaction chamber and connecting the third conduit to a separate outlet conduit.

21. **(Original)** The method according to Claim 1, further comprising the steps of connecting a second inactive gas source to an inlet of the first reactant source and using inactive gas from the second inactive gas source as a carrier gas for the first reactant.

22. **(Original)** The method according to Claim 1, further comprising the steps of connecting the inactive gas source to an inlet of the first reactant source and using inactive gas from the second inactive gas source as a carrier gas for the first reactant.

23. **(Original)** The method according to Claim 1, further comprising the steps of draining substantially all of the first reactant from the reactant source through the third conduit to between the repeated alternating pulse of the first reactant.

24. **(Original)** The method according to Claim 1, further comprising the steps of providing a condensation vessel and connecting the condensation vessel to the third conduit and condensing vaporized reactant residues in the condensation vessel.

25. **(Original)** The method according to Claim 1, further comprising connecting a second inactive gas source to the third conduit via a fourth conduit and feeding inactive gas into the third conduit.

26. **(Original)** The method according to Claim 25, further comprising using the inactive gas fed into the third conduit via the fourth conduit to reduce an amount of gas withdrawn from the first conduit.

27. **(Original)** The method according to Claim 1, further comprising connecting the inactive gas source to the third conduit via a fourth conduit and feeding inactive gas into the third conduit.

28. **(Original)** The method according to Claim 27, further comprising using the inactive gas fed into the third conduit via the fourth conduit to reduce an amount of gas withdrawn from the first conduit.

29. **(Original)** The method according to Claim 28, further comprising feeding the inactive gas into the third conduit via the fourth conduit when the first reactant is being fed into the reaction chamber, wherein the inactive gas is fed during pulsing of the reactant.

30. **(Original)** The method according to Claim 1, further comprising connecting the inactive gas source to the third conduit via a fourth conduit upstream of a flow restrictor and feeding inactive gas into the third conduit.

31. **(Original)** The method according to Claim 1, further comprising feeding inactive gas into the reaction chamber in-between the repeated alternating pulses of the first reactant.

32. **(Original)** The method according to Claim 1, further comprising the steps of alternately, with respect to the first reactant, transferring a second reactant into the reaction chamber and allowing the second reactant to react with the surface of the substrate in the reaction chamber.

33. **(Original)** The method according to Claim 1, further comprising the steps of:

- providing a second reactant source;
- transferring a second reactant from the second reactant source to the reaction chamber via a fourth conduit;
- alternately, with respect to the first reactant, allowing the second reactant to react with the surface of the substrate in the reaction chamber;
- feeding inactive gas from the inactive gas source into the fourth conduit via a fifth conduit that is connected to the fourth conduit at a third connection point so as to create a second gas phase barrier between repeated alternating pulses of the second reactant entering the reaction chamber; and
- withdrawing the inactive gas from said fourth conduit via a sixth conduit connected to the fourth conduit at a fourth connection point.

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(Application(s) filed herewith Execution Date(s):

(Patent Application Nos and Filing Dates:
See Attached Appendix A

(Patent Nos. and Issue Dates:
See Attached Appendix A

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5. Name and address of party to whom correspondence concerning document should be mailed:

Name: Andrew N. Merickel
KNOBBE, MARLENS, OLSON & BEAR, LLP
Customer No. 20,995
Internal Address: Fourteenth Floor
Street Address: 2040 Main Street
City: Irvine State: CA ZIP: 92614
Attorney's Docket No.: ASMMC.059GEN

7. Total fee (37 CFR 1.21(h)): \$40 x 60 = \$2,400

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6. Total number of applications and patents involved: 60

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Andrew N. Merickel
Name of Person Signing

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ASSIGNMENT

WHEREAS, ASM Microchemistry OY, a Finnish corporation having offices at Kutojantie 2B, 02630 Espoo, Finland (hereinafter "ASSIGNOR"), represents that it has certain right, title and interest in the United States issued Letters Patents and applications for Letters Patents in the United States (hereinafter "the Patents and Patent Applications") recited on Appendix A, attached hereto, and in the inventions disclosed therein.

WHEREAS, ASM International N.V., a Netherlands corporation having offices at Jan van Eycklaan 10, 3723 BC Bilthoven, THE NETHERLANDS (hereinafter "ASSIGNEE") desires to purchase the entire right, title, and interest in and to the inventions disclosed in the Patents and Patent Applications;

NOW, THEREFORE, in return for good and valuable consideration, the receipt of which is hereby acknowledged, ASSIGNOR hereby further acknowledges that it has sold, assigned, and transferred, and by these presents does hereby sell, assign, and transfer, unto ASSIGNEE, its successors, legal representatives, and assigns, any right, title, and interest that ASSIGNOR has throughout the world in, to, and under the said inventions, and the said Patents and Patent Applications and all Patents that may be granted thereon, and all provisional applications relating thereto, and all divisions, continuations, reissues, reexaminations, renewals, and extensions thereof, and all rights of priority under International Conventions and applications for Letters Patent that may hereafter be filed for said inventions or for the said Patents and Patent Applications in any country or countries foreign to the United States; and ASSIGNOR hereby authorizes and requests the Commissioner of Patents of the United States, and any Official of any country foreign to the United States, whose duty it is to issue patents on applications as aforesaid, to issue all Letters Patents for said inventions and all Letters Patents resulting from the Patents and Patent Applications to ASSIGNEE, its successors, legal representatives, and assigns, in accordance with the terms of this Agreement.

ASSIGNOR does hereby sell, assign, transfer, and convey to ASSIGNEE, its successors, legal representatives, and assigns all claims for damages and all remedies arising out of any violation of the rights assigned hereby that may have accrued prior to the date of assignment to ASSIGNEE, or may accrue hereafter, including, but not limited to, the right to sue for, collect, and retain damages for past infringements of the said issued Letters Patents;

ASSIGNOR hereby covenants and agrees that it will communicate to ASSIGNEE, its successors, legal representatives, and assigns any facts known to ASSIGNOR respecting the Patents and Patent Applications immediately upon becoming aware of those facts, and that it will testify in any legal proceeding involving any of the Patents and Patent Applications, will sign all lawful papers, execute all divisional, continuing, and reissue applications, make all rightful oaths, and will generally do everything possible to aid ASSIGNEE, its successors, legal representatives, and assigns to obtain and enforce the Patents and Patent Applications in all countries.

IN TESTIMONY WHEREOF, I hereunto set my hand and seal this 26 day of November, 2003

ASM Microchemistry OY

By: J. Oeler J. Oeler

Name Printed: ILKKA T. OELER

Title: MANAGING DIRECTOR

Mr. B. J. Oeler

Witness Signature

APPENDIX A

Client Code: ASMMC059GEN

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PATENTS			
SERIAL NO.	DATE FILED	PATENT NO.	ATTN. DOCKET NO.
09/686,613	1/4/00	6,630,030	SEPP1.001CP1
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Client Code: ASMMC.059GEN

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ALD precursor chemistry: Evolution and future challenges

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Abstract: The requirements of ALD precursors differ from those of CVD concerning thermal stability, adsorption on the surface, and reactions towards each other. In the first ALD experiments in the 70s elements (Zn, Cd, S), metal halides and non-metal hydrides (H_2O , H_2S) were used. In the 80s the selection of precursors widened to metal complexes (alkoxides, β -diketonates) and simple organometallics (alkyl compounds). In the 90s both new metal (Cp-compounds, alkylamides) as well as non-metal precursors (H_2O_2 , O₃, hydrazine) have been introduced. A characteristic feature of ALD is that surface groups play an important role as reactive sites for the next precursor pulse. The development of ALD precursors is limited by the small number of groups working in the field. It seems, however, that the precursor development is diverged and tailored molecules are designed for each process.

1. INTRODUCTION

Atomic Layer Deposition (Epitaxy) developed in the early 70s is a modification of CVD and can also be called as "alternately pulsed-CVD" [1,2]. Gaseous precursors are introduced one at a time to the substrate surface and between the pulses the reactor is purged with an inert gas or evacuated. In the first reaction step the precursor is saturatively chemisorbed at the substrate surface and during the subsequent purging the excess of the precursor is removed from the reactor. In the second step the other precursor is introduced on the substrate and the desired film growth reaction takes place. After that the reaction byproducts and the precursor excess are purged out from the reactor. When the precursor chemistry is favourable, *i.e.* the precursors adsorb and react with each other aggressively, one ALD cycle can be performed in less than one second in properly designed flow type reactors.

The striking feature of ALD is the saturation of all the reaction and purging steps which makes the growth self-limiting. This brings the large area uniformity and conformality, the most important properties of ALD, as shown in very different cases, *viz.* planar substrates [3], deep trenches [4] and in the extreme cases of porous silicon [5] and high surface area silica and alumina powders [6,7]. Also the control of film thickness is straightforward and can be made by simply calculating the growth cycles. ALD was originally developed to manufacture luminescent and dielectric films needed in electroluminescent displays [8] and a lot of effort has been put to the growth of doped zinc sulfide and alkaline earth metal sulfide films [9]. Later ALD has been studied for the growth of different epitaxial III-V [10,11] and II-VI [12,13] films, non-epitaxial crystalline or amorphous oxide [14,15] and nitride [16,17] films and their multilayer structures. Minor attention has been given to grow other films like those of metals and fluorides [18]. There has been considerable interest towards the ALE growth of silicon and germanium films but due to the difficult precursor chemistry the results have not been very successful [19,20].

2. REQUIREMENTS FOR THE ALD PRECURSORS

The precursors maybe gaseous, liquid or solid and in the last two cases the requirement is that they must be volatile. The vapor pressure must be high enough for effective mass transportation. The solids and some

liquids need to be heated inside the reactor and introduced through heated tubes to the substrate. The necessary vapor pressure must be reached at a temperature below the substrate temperature to avoid condensation of the precursors on the substrate.

The self-limiting growth mechanism of ALD makes it easy to use also relatively low vapor pressure precursors though their evaporation rates may somewhat vary during the process because of changes in surface area. The technologically challenging task of pulsing precursors evaporated at high temperature is solved elegantly by inert gas valving [2,3]. A challenge remaining with very small particle size solids is to prevent the particles from being transported by the carrier gas and entering the films.

The precursors must be thermally stable at the substrate temperature because their decomposition would destroy the surface control and accordingly the advantages of the ALD method. A slight decomposition, slow compared to the ALD growth, is acceptable as shown in the case of metal alkoxide precursors for growth of oxide films [21,22].

The precursors have to chemisorb on or react with the surface. The interaction between the precursor and the surface as well as the mechanism of the adsorption is different for different precursors as will be pointed out later on. The adsorption can in the most cases be considered as an exchange reaction as reported in the growth of oxide films where the surface OH groups play an important role [23,24]. After purging the molecule at the surface has to react aggressively with the second precursor and form the desired solid film. The demand of highly reactive precursors in ALD is in marked contrast to the selection of precursors for conventional CVD. The aggressive reactions guarantee effective use of precursors, short pulse times and purity of the films in ALD. Thermodynamic considerations of the film formation reactions are useful although the dynamic conditions in the process do not completely fulfill the real equilibrium requirements. The aggressive reaction desired means that reactions having large negative values of ΔG are looked for. Useful programs for calculations exist [25] but unfortunately thermodynamic data are not available for a large number of organometallic precursors. The ΔG value is only tentative since it tells about the spontaneity of the reaction between the gaseous precursor molecules but nothing on the kinetics and, more importantly, nothing on adsorption. If there is no site where the precursors can adsorb and be anchored, the growth can not take place. There is no thermodynamic data for calculation and prediction of adsorption and surface reactions and therefore to get predictions of them extensive quantum chemical calculations are needed. The requirement for a negative ΔG is not strict since the growth proceeds under dynamic conditions where the by-products are removed from the surface. The reaction between InCl_3 and water to In_2O_3 has been successfully utilized in ALD although its ΔG is slightly positive [26].

The side-products in the reaction must be gaseous in order to allow their easy removal from the reactor. The side-products should not further react or adsorb on the surface. The reaction between metal chlorides and water, often used in the ALD growth of oxide films, produces HCl which may readSORB or react and cause lowering of the growth rate or inhomogeneity in film thickness as shown in the case of TiO_2 , for example [23,27,28]. HCl has been shown to adsorb also on the alumina and undergo an exchange reaction between the OH group, most readily with the basic ones [29].

Precursors should not react with the film and cause etching. NbCl_5 is an extreme example since it reacts with niobium oxide and volatile oxochlorides are formed hindering the film growth [30]. TaCl_5 behaves slightly similarly but the etching is not so severe and Ta_2O_5 film can be grown in a self-limiting manner below the temperature where the etching begins, about 275°C [31].

The final requirement for the precursor is that it should not dissolve in the film. This rather rare situation was observed when copper films were grown using zinc vapor as a reducing agent. Zinc dissolved in copper forming brass. During purging and the next copper precursor (CuCl) pulse zinc was re-evaporated and an uncontrolled copper formation reaction took place [32].

While integrating ALD processes for making complete devices, the compatibility of the precursors with the underlying material, substrate or film, must be taken into account. No etching, harmful reactions or dissolution may take place.

and tubes to the substrate, substrate temperature to avoid

relatively low vapor pressure process because of changes in evaporated at high temperature by small particle size solids in patterning the films.

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action between the precursor parent precursors as will be pointed out as reported in the role [23,24]. After purging to the selection of precursors for precursors, short pulse times in ion reactions are useful although equilibrium requirements. The values of ΔG are looked for. Useful data are not available for a large part it tells about the spontaneity, kinetics and, more importantly, and be anchored, the growth kinetics of adsorption and surface calculations are needed. The dynamic conditions where the and water to In_2O_3 has been

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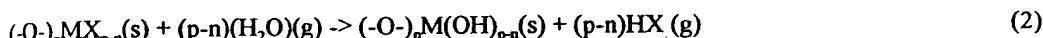
3. PRECURSOR COMBINATIONS AND SURFACE AS A REACTANT

The unique features of ALD are not that much reflected in the choices of single precursor molecules which are essentially the same as those used in CVD. Rather, it is the way how they are combined (Table 1) which makes the difference. As mentioned above, the precursors must react aggressively and completely. The difference to CVD chemistry is clear since ALD favours precursor combinations, for example trimethylaluminium (TMA) + water, zinc chloride + hydrogen sulfide, which in CVD can not be mixed together and introduced simultaneously into the reactor.

The surface chemistry of ALD relies on either molecular chemisorption or, perhaps more often, reaction of the incoming precursor with the functional group on the surface. Experimental evidences of the latter case have been reported in many papers on ALD oxide films using water as an oxygen precursor [17,23,24, 33,34]. There the actual reaction takes place between the OH groups on the surface and the metal precursor:



where M is a metal ion, X is a ligand, typically halide, alkoxide or alkyl. p varies depending on the metal and ligand and n varies depending on the amount of surface hydroxyl groups which in turn is a function of temperature. During the next pulse water changes the surface to a hydroxylated one:



The correlation between the amount of hydroxyl groups on the surface and the amount of metal precursors adsorbed has been shown in the experiments made on high surface area silica powder [33]. Also the low growth rate of In_2O_3 thin films, known to be deficient of surface OH groups, can be explained by the lack of reaction sites during the indium precursor pulse [34]. On the other hand, the increase of the water dose in a pulse significantly increases the growth rates of oxide films which can be understood in terms of increased hydroxyl group densities [35].

The lack of anchoring sites or functional groups can be the reason for the non-ideal results obtained for example with III-V compound and elemental (metal) films. On the other hand, ALD growth on selective sites could be utilized in selective area growth experiments by patterning the OH terminated surface and growing the film on the OH covered areas only. Crystallographically selective area growth is also possible as shown by Isshiki et al. [36,37]. They grew epitaxial III-V films and by controlling purging times they were able to deposit GaAs and GaP films either selectively on the (100) surfaces only or simultaneously on both the (100) and (111) surfaces of their (100)GaAs substrates which contained V-shaped grooves with the (111) oriented sidewalls.

Direct experimental evidences on molecular chemisorption in ALD are sparse. Real time quartz crystal microbalance (QCM) measurements can be used to monitor the relative masses of adsorbed species [38]. Most processes studied by this method involve metal chlorides and water precursors and are aimed for oxide films, and also in the studies on β -diketonato complexes water has been used as the oxygen precursor. Thus the effect of OH groups is present in the adsorption which involves partial release of the β -diketonato ligands [39,40]. Kawai and coworkers [41,42] have shown, however, that $Cu(thd)_2$ and $Ca(thd)_2$ can chemisorb on silica surface without exchange reaction via the interaction between surface oxygen atoms and C-O bonds in the complex.

4. PRECURSORS USED

The need to develop a new deposition method for electroluminescent (EL) thin film devices which require high-quality, pinhole-free dielectric and luminescent films deposited on large area glass substrates resulted in the discovery of the ALD method [8]. In the monochrome yellow-emitting EL devices $ZnS:Mn$ thin films

are used as the phosphor material. Therefore, the first experiment carried out used elemental zinc and sulfur as precursors and that is the origin of the name Atomic Layer Epitaxy. When grown on single crystal substrate at high enough temperature, real epitaxy can be obtained. Soon it turned out that molecular precursors ($ZnCl_2$, $MnCl_2$, H_2S) are more convenient to handle and films of the quality needed in EL devices can be achieved. For these reasons and because only a few of them are volatile enough, elements are rarely used as precursors, II-VI compounds being the exceptions (Table 1). Epitaxial CdTe has been grown on (100) GaAs in a monolayer fashion at a limited temperature range (260-290 °C) and at higher temperatures 0.5 ML/cycle growth was achieved [43]. With ZnSe the process window for 1 ML/cycle is wider, viz. 250-350 °C [44]. The use of elemental zinc as a reducing agent in the ALD growth of transition metal nitrides is also worth mentioning [14,16,18].

In the following the ALD precursor chemistry is highlighted according to different precursor types. Table 1 summarizes the different precursors and reactions used in ALD without references. For detailed references the recent reviews [15,45,46] are referred to.

4.1 Precursors for non-metals

4.1.1 Oxygen

Water has been by far the mostly used precursor chemical for oxygen. It reacts fast with many metal halides and alkyls and reasonably well with metal alkoxides forming via surface hydroxyl groups oxide films as described above. Problems with water arise with β -diketonato complexes because the reaction does not occur or is slow at temperatures below 500 °C. In CVD β -diketonates have been used together with oxygen but usually the temperature has been rather high [47]. Y_2O_3 films are the only ones reported to be grown by ALD from β -diketonates ($Y(thd)_3$) and O_2 with a low rate of 0.2 Å/cycle [48]. The inertness of the O_2 molecule can be explained by the double bond and accordingly all burning reactions need high temperatures. The use of ozone instead of oxygen makes the ALD growth of oxides from the β -diketonates faster but slightly non-ideal since no ALD-window can be found but the growth rate increases with increasing temperature [48,49].

H_2O_2 has been in few difficult cases (In_2O_3 , SiO_2) used instead of water to improve the growth rate [50,51]. The improvement can be explained by the increased number of OH groups on the surface. H_2O_2 reacts also with TMA more eagerly than water but at low temperatures the resulting Al_2O_3 films are not very dense as is the case also when water is used [52]. Alcohols have been used as oxygen precursor in deposition of Al_2O_3 films from both $AlCl_3$ and different alkoxides [53].

4.1.2 Sulfur and selenium

Hydrogen sulfide is a suitable and the mostly used sulfur precursor in ALD. It reacts well with very different metal precursors: halides, alkyls, carboxylates, β -diketonates and cyclopentadienyl compounds (Table 1). H_2S is used in the large scale production of ZnS based and pilot scale production of SrS based EL phosphors. Quantum chemical calculations on the reaction $ZnCl_2 + H_2S \rightarrow ZnS$ have shown that the interaction of H_2S on $ZnCl_2$ surface is dependent on the arrangement of the $ZnCl_2$ molecules. Independently chemisorbed $ZnCl_2$ molecules favour additive reaction of H_2S and the critical step is the formation of HCl while $ZnCl_2$ chains favour the immediate reaction to ZnS [54,55]. A mass-spectroscopic study of the same reaction showed that HCl is released only after the H_2S pulse and not after the $ZnCl_2$ pulse [56].

The reaction between dimethyl zinc and H_2S proceeds in a monolayer fashion at 250-310 °C [57]. The process is sensitive to H_2 purge and $Zn(CH_3)_2$ dose. It is proposed that dimethyl zinc adsorbs as a molecule on the sulfur surface. The H_2 sensitivity gives indications for the possibility of an inhibiting reaction where

used elemental zinc and when grown on single crystal it turned out that molecular quality needed in EL is not enough, elements are essential CdTe has been grown [56] and at higher temperatures ML/cycle is wider, viz. μ th of transition metal nitrides. For different precursor types references. For detailed reference

fast with many metal halides. Hydroxyl groups oxide film because the reaction does not used together with oxygen reported to be grown [48]. The inertness of the ions need high temperatures the β -diketonates faster but increases with increasing

to improve the growth rate groups on the surface. H_2O using Al_2O_3 films are not very good precursor in deposition

acts well with very different phenyl compounds (Table 1) of SrS based EL phosphors that the interaction of H_2S with indented chemisorbed $ZnCl_2$ instead of HCl while $ZnCl_2$ chains same reaction showed that

on at 250-310 °C [57]. The zinc adsorbs as a molecule in inhibiting reaction where

metallic zinc and methane are formed [57]. A recent detailed study on $Cd(CH_3)_2 + H_2S$ ALE reactions showed, however, that dimethyl cadmium chemisorbs dissociatively releasing methane and forming a monomethylated surface [58]. Methane is also released during the H_2S pulse and a SH surface is formed. The mechanism proposed where the surface SH groups play an important role resembles closely to that reported for water and surface OH groups.

Hydrogen selenide reacts like hydrogen sulfide with zinc chloride and alkyl compounds forming $ZnSe$. The studies have been focused on verifying the ML growth/cycle and details of the mechanisms and the possible role of SeH groups have not been reported. The use of a thermal precursor cracker improves the film quality and has been explained by the formation of elemental species having surface mobility higher than $Zn(C_2H_5)_2$ and H_2Se [59].

4.1.3 Nitrogen

Ammonia has automatically been the precursor for nitride films. Three types of approaches have been taken towards nitride films: epitaxial GaN ($Al_{1-x}Ga_xN$, $Ga_{1-x}In_xN$) films grown from alkyl compounds and ammonia for optoelectronic applications [60], polycrystalline AlN films for dielectric and passivation layers [61] and polycrystalline transition metal nitrides (TiN , NbN , TaN , Ta_3N_5 , MoN) grown from metal chlorides for diffusion barrier and protective applications [14]. In systems where no reduction of the metal (Al , Ga , In) is needed ammonia works rather well. The impurities found from for example AlN films: chlorine and hydrogen with $AlCl_3$ [61, 62] and carbon and hydrogen with TMA [62], show that ammonia leaves behind some hydrogen. The oxygen found in the AlN films is concentrated on the surface indicating post deposition oxidation. Volatile transition metal precursors usually contain metals at their highest oxidation states but in the nitrides the oxidation state is +III and therefore reduction must occur. Ammonia is reducing in nature and for example TiN can be prepared with the reaction between $TiCl_4$ and NH_3 , and the film made at 500 °C is rather pure but films of better conductivity are obtained if zinc is used as an additional reducing agent [16]. Ammonia does not reduce $TaCl_5$ and Ta_3N_5 is formed, and Zn vapour reduction is needed for TaN [63, 64]. As a summary, ammonia is a suitable precursor for nitride formation reactions with metal chlorides if the metal ion has not to be reduced. If reduction is needed an additional reducing agent may be necessary. The situation may change if other metal precursors than chlorides are used as shown in the case of TiI_4 [65].

4.1.4 Hydrides of Group V (15) Elements

PH_3 , AsH_3 and SbH_3 are the most common precursors for the group V elements. In ALE they have been used together with both chlorides and alkyl compounds of the group III elements (Table 1). The ALE growth of the III-V compounds has not been very successful because of the complexity of the surface chemistry and there is no single mechanism for the growth of the III-V compounds by ALE. The difficulties in the surface chemistry are believed to be mainly due to the group III precursors and not because of the group V hydrides. However, the As-H species play certainly an important role in the chemisorption of TMG and the instability of surface AsH_3 is a partial reason for the problems. Fast injection of AsH_3 , high hydrogen partial pressure and injection of atomic hydrogen on AsH_3 surface have improved the self-limiting type growth [45]. However, in some experiments wide temperature, pulse time and pressure windows have been observed [66] and they must be addressed to the ligand exchange reactions similar to those described for the growth of oxide films. The precursors for the group V elements are not under special development but the users are satisfied to the compounds commercially available for MOVPE.

4.1.5 Fluorine

The only paper existing on the ALD of fluoride films reports the use of NH_4F as a precursor for $\text{Ca}_x\text{Sr}_{1-x}\text{Zn}$ fluorides [67]. The precursor is not ideal and the growth rate remains low. In deposition of SrSr_xGe_y fluoride codoping has been performed by benzoyl fluoride which is a suitable precursor for codoping but not for growing bulk fluoride films [68].

4.2 Metal precursors

4.2.1 Halides

Metal halides, especially chlorides, are applicable precursors in ALD deposition of oxide, sulfide and nitride films. They are volatile and reactive enough but most of them are solids which is in microelectronic industry considered as a disadvantage. The ALD surface chemistry of chlorides has been studied thoroughly both on planar substrates and on high surface area oxide powders in preparation of oxides. As described above in those cases metal chlorides are reacting with surface OH groups and HCl is formed. Much less is known on the chemisorption on sulfur surfaces. The calculations show that ZnCl_2 adsorbs on sulfur surface form a stable complex [54,55] though desorption of ZnCl_2 may occur easily [56]. Due to the size of the chloride anions and their repulsion, maximum surface coverage can be either $1/3$ or $1/2$ depending on whether the adsorption mode is independent or chain-like, respectively. Experimentally it has been shown that 2-3 cycles are needed for one monolayer depending on the experimental conditions [69]. The role of surface SH groups has not been studied in detail.

The behaviour of aluminium, gallium and indium trichlorides in the growth of oxide films differs from each other markedly: Al_2O_3 can be grown with a good rate, Ga_2O_3 does not grow at all, In_2O_3 grows with a low rate. The oxide formation reactions become thermodynamically more unfavored in the same order. Partially those behaviours can possibly be addressed to the stability of OH groups on the oxide surface. The reactivity of Al, Ga and In chlorides with ammonia follows the same trend as that with water. In GaAs ALE GaCl has been more often studied as a precursor than GaCl_3 . The reaction between GaCl and AsH_3 is not very favorable and long pulsing times are needed, and on the other hand GaCl desorption may occur and GaCl surface may change to inert Ga surface [70]. The studies have shown that GaCl reacts with As_4 precursor only in the presence of hydrogen [71]. A rather wide 1 ML/cycle ALE window has been found for $\text{GaCl}_3 + \text{AsH}_3$ and the suggestion for the reaction mechanism goes via AsH and $\text{As}-\text{GaCl}_2$ surface species [72].

SiCl_4 reacts with water producing SiO_2 films. The reaction is, however, very slow and pulse times of tens of seconds are needed. The process relies on the surface OH groups and the growth rate is dependent on temperature which further determines the OH content on the surface [73]. The reaction can be enhanced by pulsing pyridine after each reactant pulse. Both the reaction temperature and pulse times could be reduced significantly without losing the growth rate per cycle and the quality of the film [74].

4.2.2 Alkyl compounds

Because of the importance of the III-V semiconductors most ALE and ALD studies using alkyl precursors deal with Ga, Al and In. Both trimethyl and triethyl compounds are easily available and their chemistry in CVD is known. No special precursor for ALE has been designed. The ALE deposition of GaAs has been studied by numerous groups using different experimental set-ups and very different results have been reported. The difficulties arise from the instability of Ga alkyl compounds (mainly trimethyl gallium, TMG). In ultra high vacuum systems no saturative growth or a very narrow temperature range for the saturation

has been observed but the saturation can be enhanced by laser irradiation [45]. The use of high-speed flow in a hydrogen transport has resulted in reasonably wide saturation range [66,75].

Three models have been suggested for the ALE GaAs surface chemistry. First, the TMG converts the arsenic-terminated surface to a gallium-terminated one and the methyl groups desorb. This surface is no longer reactive towards TMG [76]. Second, TMG reacts with arsenic surface and forms a gallium rich surface covered with methyl groups. The methyl groups make the surface passive for further adsorption of TMG [77]. Third, TMG (or TEG) decomposes on the surface to a monomethyl (ethyl) species which desorbs from the surface and no deposition takes place. The growth requires a flux balance between the adsorbing and desorbing species [78]. As a conclusion it can be said that ideal saturative growth is hard to achieve by TMG (TEG) and arsine.

The behaviours of Al and In alkyls are similar to those of gallium alkyls in the growth of the III-V compounds. AlAs and InP are the most commonly studied materials after GaAs. By using different tricks in time scales, flow rates, precursor cracking, and H₂ purges it has been possible to grow these materials 1 ML/cycle in a limited temperature range [45]. In the growth of oxide films the alkyl compounds behave like chlorides: TMA + H₂O is almost an ideal reaction [79,80], TMG + H₂O does not proceed at all and TMI + H₂O shows extremely low growth rate [34]. TMA-water process works in a wide temperature range (100-500 °C) but the OH (or H) content of the film increases with decreasing temperature. The process has been studied in many applications including modification of catalyst supports and membranes [81], dielectric films for EL devices and corrosion protection films. The reaction of Al and Ga alkyl compounds with ammonia results in AlN and GaN [60,62]. Clear temperature window for the self-limiting growth does not exist but stable growth can be achieved at fixed temperature.

Dimethyl (DMZ) and diethyl (DEZ) zinc have been used in deposition of both epitaxial ZnS and ZnSe films as well as polycrystalline ZnS and ZnO films. Close to 1 ML/cycle growth was observed in the reaction between DMZ and H₂S at 25-500 °C [82]. The process can also be used in a large scale to fabricate ZnS:Mn based EL devices [83]. Both DMZ and DEZ react vigorously with water forming ZnO at 100-250 °C the ALD growth rate being reaction temperature dependent [84]. This and the observation that the reactions between DMZ and H₂S and H₂Se are hydrogen pressure dependent indicate thermal instability of the zinc alkyl compounds, not to forget the role of surface OH, SH and SeH groups, however. If the decomposition is complete and a zinc surface is formed, the chalcogenide formation reaction is inhibited.

4.2.3 Alkoxides

Alkoxides which are well known precursors in CVD have only in a few cases used in ALD (Table 1) to grow oxide films. Water and alcohols have served as oxygen precursors [21,53]. Alkoxides have a tendency to decompose at high temperatures and therefore ALD processes are limited to temperatures below 400 °C where the growth is an ALD-type exchange reaction utilizing surface OH groups. The size of the precursor molecules affects the growth rate and in the case of TiO₂ the precursor affects also the crystallinity [21,85]. Alkoxides are very important precursors for Nb and Ta oxides because their chlorides etch the forming oxides [86,87].

4.2.4 β -diketonato complexes

Electropositive metals have not many volatile compounds and β -diketonato complexes are among the few ones. The need of volatile alkaline earth and rare earth metal compounds for CVD deposition of high temperature oxide superconductors boosted the studies on β -diketonato complexes. In ALD the main interest has been in deposition of SrS based EL phosphors and thd-chelates (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione) are used as the precursors [88]. The instability of the precursors may cause some thickness non-uniformity for the films and the difficulties increase in the series Ca < Sr < Ba [89]. Anyway, Sr(thd)₂ is used in a pilot scale for SrS EL films [90].

The alkaline earth β -diketonato complexes may oligomerize which limits the volatility and the neutral adducts have been added to the complexes to keep them monomolecular. The complexes may age by reacting with moisture also resulting in oligomers. The adduct molecules are believed to be stable against aging as well [47,91]. ALD depositions of alkaline earth sulfide films have been carried out with adducted thd complexes but it seems that the neutral adduct molecules do not stay intact at the temperatures [92,93]. Thus the surface reaction is basically the same as in the case of non-adducted complexes. One other way to avoid the aging and possible decomposition of the β -diketonato complexes is to make them *in situ* in the ALD reactor. This is possible by introducing Hthd vapor over heated alkaline earth metal or hydroxide and a reasonable growth rate (0.8-1 Å/cycle) is achieved [94]. The vaporization of the Hthd liquid inside the ALD reactor requires careful temperature control but this can be avoided by pulsing Hthd from outside of the ALD reactor [95].

As mentioned above the ALD deposition of oxide films from β -diketonato complexes and water is not a favourable reaction the deposition of MgO being an exception but with a low deposition rate [96]. The best results have been obtained by using ozone as an oxygen precursor. Even ternary LaCoO₃ and LaNiO₃ which usually are difficult to prepare by CVD techniques have been grown by ALD from the corresponding thd complexes and ozone [97,98].

Cu(thd)₂ is a possible precursor for deposition of metallic copper. The reduction is made by H₂ and due to the instability of the precursor the process is self-limited only in the temperature range 190 to 260 °C. The initiation of the growth is not straightforward and a Pt/Pd seed layer is needed [99,100]. Cu(thd)₂ as well as many rare earth thd-chelates have been employed as precursors for doping ZnS or SrS based EL phosphor films [101].

The adsorption of several transition metal thd-complexes on high surface area powders have been studied in detail [102]. In adsorption on oxide surface the thd-chelate undergoes an exchange reaction between the surface OH groups. The number of metal atoms on the surface is a function of the OH group concentration (calcination temperature) and the size of the molecule. There is one recent example of molecular adsorption of a β -diketonate chelate on silica surface, *viz.* Cr(acac)₃ (Hacac = 2,4-pentanedione). The molecular adsorption occurs only at a limited temperature range 160-200 °C, however [103].

4.2.5 Cyclopentadienyl compounds

Magnesium and few other cyclopentadienyl (Cp) compounds are known as oxide precursors in CVD. Also some metal films have been grown by CVD from the cyclopentadienyl compounds. In ALD the first report on these precursors is that of Huang and Kitai [104] on MgO films. Our interest towards the Cp compounds stems from the need to find volatile compounds for the heavier alkaline earth metals capable to react with water to oxide at reasonable temperatures. Because the experiments with β -diketonates failed Cp compounds, though considered to be very sensitive to oxygen and moisture, were chosen. In practice, however, these compounds turned out to be more stable than expected and could even be shortly exposed to air. Not much attention has been paid on the growth of binary oxide (SrO, BaO) films but more importantly ternary SrTiO₃ and BaTiO₃ compounds were grown with Ti alkoxide as a titanium source. The depositions on glass substrate follow the principles of ALD: the films are polycrystalline, the composition can be affected by changing the pulse ratio of the metal precursors, thickness is uniform and depends linearly on the number of the growth cycles, and the conformality of the films is perfect [105]. Cp compounds form a big family of precursors since the ligands can be varied by substitutions in the carbon 5-ring, largening the ring system (indene, fluorene) and by linking two ring systems together by a bridge. The potential of the Cp compounds as precursors for alkaline earth metals is still largely unknown. Metallocenes of the group 4 metals (Ti, Zr, Hf) are well-known in polyolefin catalysis and they are volatile compounds which react readily with water. Thus, these are also potential ALD precursors for TiO₂, ZrO₂ and HfO₂ films.

Sr((i-prop)₂Cp)₂ reacts also with H₂S forming SrS film. The benefit of this precursor is that temperatures below 200 °C can be used to fabricate crystalline films with high growth rates [106]. In luminescent EL films

its low volatility and in particular. The complexes formed by the molecules are believed to decompose and have been carried out. The complexes do not stay intact at all, in the case of non-addition of the β -diketonato complex by introducing Hthd with a growth rate (0.8-1 Å/cycle) which requires careful temperature control [95].

to complexes and water as a deposition rate [96]. The precursors are LaCoO_3 and LaNiO_3 , which are formed from the corresponding oxides.

reaction is made by H_2 and the temperature range 190 to 260 °C is used [99,100]. $\text{Cu}(\text{thd})_2$ as well as ZnS or SrS based EL phosphors

oxides have been studied. The exchange reaction between the OH group concentration and the example of molecular adsorption of pentanedione. The molecular

xide precursors in CVD. Also compounds. In ALD the first report is towards the Cp compounds of metals capable to react with H_2 . β -diketonates failed Cp, were chosen. In practice, could even be shortly exposed to O_2 (SrO, BaO) films but more xide as a titanium source. The polycrystalline, the composition is uniform and depends linearly on the film thickness [105]. Cp compounds form a carbon 5-ring, largening the ridge. The potential of the Cp compounds is high.

Metallocenes of the group 4 compounds which react readily with HfO_2 films.

precursor is that temperatures are high [106]. In luminescent EL films

a dopant is needed and when an organometallic precursor for the dopant is a necessity, the growth temperature must be low and then the alkaline earth Cp-precursors may be a good choice.

Rare earth metals form another group of electropositive metals which have only a few volatile compounds. The rare earth β -diketonates are reasonably stable and their volatility properties are good but their reactivity with water to oxide films is low. As dopant precursors for ZnS:Ln and SrS:Ln films they can be used [101]. However, with cerium, one of the most important dopants for SrS , better results have been obtained with Cp precursors [83].

4.2.6 Carboxylato complexes

The number of known volatile carboxylato complexes is low. In ALD only zinc acetate has been used in deposition of ZnS films [107]. Zinc acetate oligomerizes to a tetramer before evaporation and the actual molecule adsorbing on the surface is $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$ and accordingly the growth rate of the film is high [106,108]. Zinc acetate can be used also as a precursor for ZnO films although the growth rate is very low.

4.2.7 Silanes and germanes

ALE deposition of silicon (and also germanium) using different silanes or chlorosilanes has extensively been studied. Special attention has been given to the adsorption of different precursors on Si surface [19,20]. The results show that the surface chemistry of the precursors used is not favourable but UV-irradiation or thermal cycling is needed for obtaining pure films. According to Gates [109] all reactions studied in ALE using two Si precursors, silane + chlorosilane, are thermodynamically unfavoured. Only those reactions which involve atomic hydrogen are spontaneous and can be considered self-limiting. It seems that reactants which can be alternately pulsed and which make the self-limiting Si growth possible are not yet known.

4.2.8 Others

There are few other precursors not mentioned above which have been used in ALD. Alkylamides, recently widely studied in CVD, have only a few times been used in ALD [110]. Isocyanate compounds of silicon ($\text{Si}(\text{NCO})_4$) form a new interesting group of precursors with which it is possible to grow SiO_2 films in a $\text{Si}(\text{NCO})_4$ / SiCl_4 ML/cycle fashion [111,112]. The pulse times have, however, been unpractical long like in the case of SiCl_4 . The development of these new precursors shows that new potential ALD precursors can be found.

5. FUTURE CHALLENGES

There are a lot of challenges and development work to be done before ALD is accepted as an important thin film deposition technology for opto- and microelectronics. As pointed out above the key role in the process development is the precursor chemistry. The first challenge is to get more chemists to work with the precursors. CVD faces the same challenge because worldwide the precursor development is not very extensive. On the other hand, there are of course more companies specializing on CVD precursors than ALD precursors. Luckily, these companies have shown increasing interest towards ALE and ALD which is a natural development recognizing the similarities of the two fields.

The areas where ALD precursor development is needed are obvious: areas where the experiments with chemicals available have not been very successful, *viz.* III-V compounds and silicon. The other areas where

precursor development is needed are at least: good reducers for reactions where oxidation states must be lowered, more efficient nitrogen source material than ammonia, new organometallic precursors for electropositive elements, stable volatile precursors for noble metals, and suitable reactant combinations for metal film depositions.

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[109] G.
[110] N.
[111] S.
[112] ↑

Table 1

Metal

Elem.

/n

CJ

Hall

AlC

Gor

Gor

Ir

h

S

(1990) L1350-161
 70 (1997) 1092-1099
 2397-2399.
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41 (1987) 548-555.

Table I. Precursors used in ALD technique. For references see the recent review papers [14,15,45,46].

Metal precursor type	Non-metal precursor	Film material grown
<i>Elements</i>		
In	S Se Se(C ₂ H ₅) ₂ Te	ZnS ZnSe ZnSe ZnTe
Cd	S Te	CdS CdTe
<i>Halides</i>		
AlCl ₃	H ₂ O, H ₂ O ₂ , O ₂ , ROH NH ₃ AsH ₃ P ₂ O ₅ (CH ₃ O) ₂ PO	Al ₂ O ₃ AlN AlAs AlPO ₄ AlPO ₄ GaAs GaP _{1-x} As _x GaN
GaCl	AsH ₃ P ₄ + As ₄ NH ₃ AsH ₃ CuCl + H ₂ S	GaAs CuGaS ₂ InP In _{1-x} Ga _x As
GaCl ₃		In ₂ O ₃ In ₂ S ₃ SiO ₂ Cl dopant in SrS
InCl	PH ₃ GaCl + AsH ₃ H ₂ O, H ₂ O ₂	TiO ₂ TiN
InCl ₃	H ₂ S H ₂ O	TiN TiO ₂ ZrO ₂ HfO ₂ NbN
SiCl ₄	H ₂ S Si ₂ H ₆ H ₂ O	Ta ₂ O ₅ Ta ₃ N ₅ TaN
Si ₂ Cl ₆		Ta ₂ O ₅ N _x
TiCl ₄	NH ₃ NH ₃ H ₂ O	MoN
TiI ₄	NH ₃ H ₂ O, H ₂ O ₂	WO ₃ Dopant in ZnS
ZrCl ₄	H ₂ O	
HfCl ₄	H ₂ O	
NbCl ₅	NH ₃	
TaCl ₅	H ₂ O	
	NH ₃ , + Zn	
	NH ₃ , + H ₂ O	
	NH ₃ , + Zn	
	H ₂ O	
	H ₂ S	

CuCl	Zn, H ₂ GaCl ₃ + H ₂ S	Cu
ZnCl ₂	H ₂ S H ₂ Se H ₂ S + Se	CuGaS ₄
CdCl ₂	H ₂ S	ZnS
SnCl ₄	H ₂ O	ZnSe
SbCl ₃	H ₂ O	ZnS _{1-x} Se _x
		CdS
		SnO ₂
		Sb ₂ O ₃

Alkyl compounds

Al(CH ₃) ₃	H ₂ O, H ₂ O ₂ , O ₂ , N ₂ O NH ₃ AsH ₃ ((CH ₃) ₂ N) ₂ As	Al ₂ O ₃ AlN AlAs AlAs
Al(CH ₃) ₂ Cl	H ₂ O NH ₃	Al ₂ O ₃ AlN
Al(CH ₃) ₂ H	PH ₃ AsH ₃	AlP AlAs
Al(C ₂ H ₅) ₃	AsH ₃ H ₂ O NH ₃	AlAs Al ₂ O ₃ AlN
Al(i-C ₄ H ₉) ₃	AsH ₃	AlAs
Ga(CH ₃) ₃	PH ₃ AsH ₃ BuAsH ₂	GaP GaAs GaAs
Ga(C ₂ H ₅) ₃	AsH ₃ BuAsH ₂ ((CH ₃) ₂ N) ₂ As	GaN GaP GaAs
Ga(C ₂ H ₅) ₂ Cl	AsH ₃	GaAs
Ga(CH ₂ C(CH ₃) ₃) ₃	AsH ₃	GaAs
In(CH ₃) ₃	PH ₃ AsH ₃ H ₂ O	InP InAs In ₂ O ₃
In(CH ₃) ₂ Cl	AsH ₃	InAs
In(C ₂ H ₅) ₃	AsH ₃	InAs
In(C ₂ H ₅) ₂ Cl	AsH ₃	InAs
In(C ₂ H ₅) ₂ (CH ₃) ₂	NH ₃	InN
Zn(CH ₃) ₂	H ₂ O H ₂ S H ₂ S + O ₂ H ₂ Se H ₂ S + H ₂ Se (C ₂ H ₅) ₂ Te CH ₃ (allyl)Te	ZnO ZnO ZnS ZnO _{1-x} S _x ZnSe ZnS _{1-x} Se _x ZnTe ZnTe
Zn(C ₂ H ₅) ₂	H ₂ O	ZnO
Cd(CH ₃) ₂	H ₂ S H ₂ S (C ₂ H ₅) ₂ Te (Pr) ₂ Te CH ₃ (allyl)Te	ZnS CdS CdTe CdTe CdS
Cd(C ₂ H ₅) ₂	H ₂ S	CdTe
Sn(CH ₃) ₄	NO ₂	CdTe
Sn(C ₂ H ₅) ₄	NO ₂	CdS SnO ₂ SnO ₂

EUROCVD 12

Alkoxides

$Al(OCH_2H_5)_3$	H_2O	Al_2O_3
$Al(OCH(CH_3)_2)_3$	H_2O, ROH	Al_2O_3
$Ti(OCH_2H_5)_4$	H_2O	TiO_2
$Ti(OCH(CH_3)_2)_4$	H_2O	TiO_2
$Nb(OCH_2H_5)_3$	H_2O	Nb_2O_5
$Ta(OCH_2H_5)_3$	H_2O	Ta_2O_5
$Pb(OBu')_2$	NH_3	TaO_xN_y
$Pb_2O(OBu')_6$	H_2S	PbS
	H_2S	PbS

 β -diketonato complexes

$Mg(thd)_2$ ^a	H_2O, O_3	MgO
	H_2S	MgS
$Ca(thd)_2$	H_2S	CaS
	NH_4F	CaF_2
$Sr(thd)_2$	H_2S	SrS
	NH_4F	SrF_2
	O_3	$SrO (SrCO_3)$
	$Ti(OPr)_4 + O_3$	$SrTiO_3$
$Ba(thd)_2$	H_2S	BaS
$Y(thd)_3$	O_3, O_2	Y_2O_3
$La(thd)_3$	H_2S	La_2S_3, La_2O_2S
	$Co(thd)_2 + O_3$	$LaCoO_3$
	$Ni(thd)_2 + O_3$	$LaNiO_3$
$Ce(thd)_4$	O_3	CeO_2
$Mn(thd)_3$	H_2S	$Dopant in ZnS$
$Co(thd)_3$	O_3	Co_3O_4
$Cu(thd)_2$	H_2	Cu
	H_2S	$Dopant in SrS$
$Pb(thd)_2$	H_2S	PbS
$Ln(thd)_3$ ^b	H_2S	$Dopants in SrS and ZnS$

^a thd = 2,2,6,6-tetramethyl-3,5-heptanedione. Alkaline earth thd-complexes used may also contain a neutral adduct molecule or they

^b thd = 2,2,6,6-tetramethyl-3,5-heptanedione. Alkaline earth thd-complexes used may also contain a neutral adduct molecule or they

may have been slightly oligomerized

^b $Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Tm$

Cyclopentadienyl compounds

$Mg(Cp)_2$	H_2O	MgO
	$Al(C_2H_5)_3 + H_2O$	$MgAl_2O_4$
$Sr((i\text{-}prop)_3Cp)_2$	$Ti(OPr)_4 + H_2O$	$SrTiO_3$
$Ba((CH_3)_3Cp)_2$	$Ti(OPr)_4 + H_2O$	$BaTiO_3$
$Mn(Cp)_2$	H_2S	$Dopant in ZnS$
$Mn(CH_3Cp)(CO)_3$	H_2S	$Dopant in ZnS$
$ZrCp_2Cl_2$	O_3	ZrO_2
$Ce(Me_4Cp)_2$	H_2S	$Dopant in SrS$

^c $Cp = C_5H_5$

Carboxylates

$Zn(CH_3COO)_2$	H_2S	ZnS
	H_2O	ZnO
	H_2S	ZnS
$Zn_4(CH_3COO)_6$	H_2O	ZnO

Hydrides

$(CH_3)_3NAIH_3$	NH_3	AlN
$(C_2H_5CH_3)_2NAlH_3$	AsH_3	AlAs
SiH_4	AsH_3	AlAs
SiH_2Cl_2	UV-light	Si
	H_2 , atomic H	Si
	C_2H_2	SiC
	$NH_3 + plasma$	Si_3N_4
	N_2H_4	Si_3N_4
Si_2H_6	UV-light	Si
	C_2H_2	SiC
	SiH_2Cl_2 , H_2 , atomic H	Si
$(C_2H_5)_2SiH_2$	heat	Si
GeH_4	UV-light	Ge
$Ge(CH_3)_2H_2$	atomic H	Ge
$Ge(C_2H_5)_2H_2$	heat	Ge

Alkylamides

$Ti(N(CH_3)_2)_4$	$NH_3 + SiH_4$	$Ti_xSi_yN_z$
$Ti(N(C_2H_5CH_3)_2)_4$	NH_3	TiN
$Ce(N(Si(CH_3)_3)_2)_3$	H_2S	Dopant in SrS

Others

$Si(NCO)_4$	H_2O	SiO_2
$CH_3OSi(NCO)_3$	H_2O_2	SiO_2
$Pb((C_2H_5)_2NCS_2)_2$	H_2S	PbS

United States Patent [19]

Manasevit et al.

[11]

4,066,481

[45]

Jan. 3, 1978

[54] METALORGANIC CHEMICAL VAPOR DEPOSITION OF IVA-VIA COMPOUNDS AND COMPOSITE

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[73] Assignee: Rockwell International Corporation, El Segundo, Calif.

[21] Appl. No.: 647,222

[22] Filed: Jan. 7, 1976

Related U.S. Application Data

[62] Division of Ser. No. 523,599, Nov. 11, 1974, abandoned.

[51] Int. Cl.² H01L 21/205; H01L 21/84

[52] U.S. Cl. 148/174; 136/89 TF; 156/610; 156/613; 156/614; 148/175; 252/62.3 S; 252/62.3 V; 357/4; 357/16; 357/30; 423/508; 423/509; 427/87; 427/90; 427/91; 427/248 B

[58] Field of Search 148/175, 174; 156/610, 156/612-614, 600, DIG. 72, 85; 252/62.35 V; 427/87, 90, 91, 248; 357/4, 16, 30; 423/508, 509; 136/89

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Primary Examiner—L. Dewayne Rutledge

Assistant Examiner—W. G. Saba

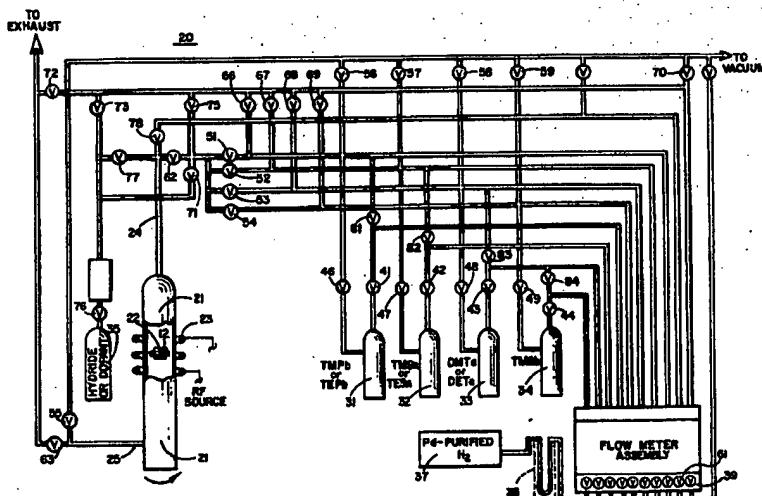
Attorney, Agent, or Firm—H. Fredrick Hamann; G. Donald Weber, Jr.; Robert Ochis

[57] ABSTRACT

A composite comprising a monocrystalline substrate and one or more layers or films of monocrystalline IVA-VIA compounds and/or alloys formed thereon by a chemical vapor deposition process. The composite is formed at a preferred temperature range of approximately 450°-650° C. The IVA-VIA layer(s) are produced by the pyrolysis of a gas mixture containing metalorganic compounds. Where single crystal metallic oxide substrates of rhombohedral structure, such as sapphire, (α -Al₂O₃), or of cubic structure, such as magnesium aluminate (spinel), are used for the growth of monocrystalline lead-containing films such as Pb_{1-x}Sn_xTe, a nucleation layer of lead is preferably formed on the substrate prior to the pyrolysis of the mixed gaseous reactants.

Using the present process, epitaxial monocrystalline IVA-VIA compounds and/or alloys can be grown on inorganic metal oxide substrates, such as cubic and rhombohedral oxides, on alkali halides and IIA fluorides, and on II-VI and III-V compounds. The compositions of the films can be varied without removing the composites from the deposition apparatus by changing the ratio of the reactant gases and the reaction temperature. The conductivity type (n-type or p-type) of the films also can be controlled without removing the composites from the deposition apparatus by varying the reactant gas compositions and by incorporating a dopant into the reactant mixtures prior to pyrolysis.

15 Claims, 3 Drawing Figures



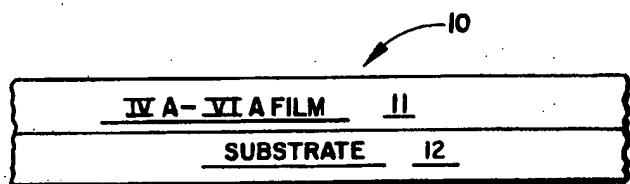


FIG. 1

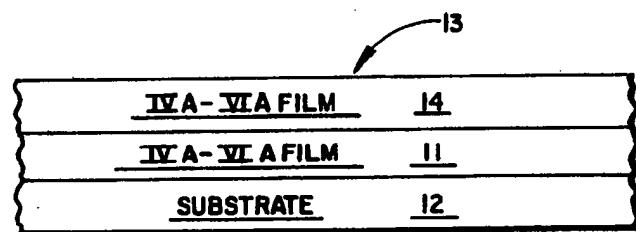


FIG. 2

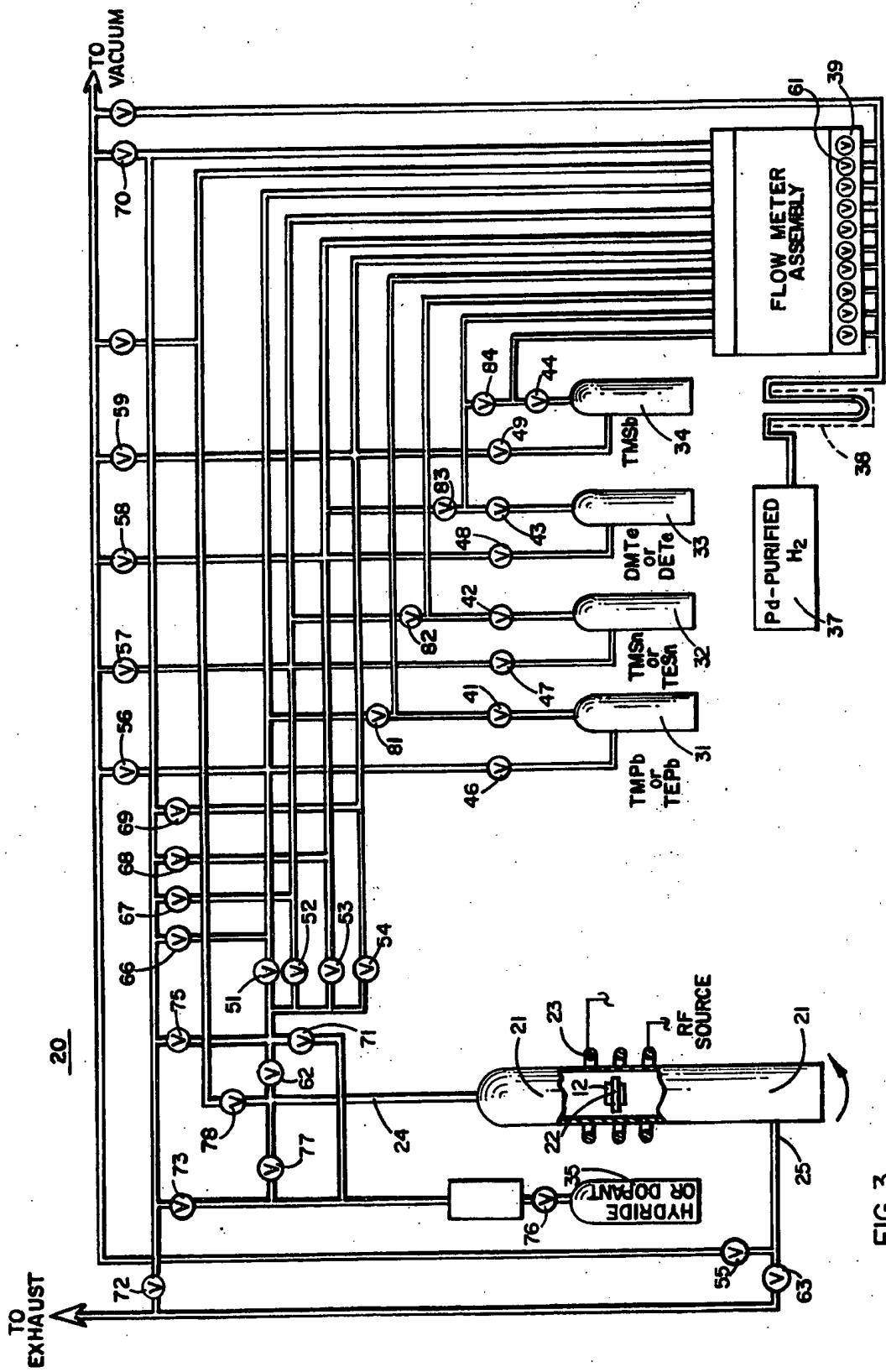


FIG. 3

**METALORGANIC CHEMICAL VAPOR
DEPOSITION OF IVA VIA COMPOUNDS AND
COMPOSITE**

The invention described herein was made in the course of or under contract or subcontract thereunder with the Department of the Army.

This is a division, of application Ser. No. 523,599 filed Nov. 11, 1974, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the growth of IVA-VIA compounds and, more particularly, to the growth of composites comprising layers of IVA-VIA compounds and alloys on substrates.

2. Description of the Prior Art

One application of IVA-VIA compounds is to infrared (IR) detectors. To date, various semiconductor materials have been used to form IR detectors, with the result that such detectors presently cover a wide range of the IR spectrum. However, past efforts have been concentrated on extrinsic semiconductors, rather than intrinsic semiconductors, because of the highly advanced technology for these materials, which is primarily the result of transistor technology.

While detectors formed from extrinsic semiconductors can exhibit high D^* and high speed, they are generally limited to operation at very low temperatures. Also, a relatively large volume of detector material is usually required in order to absorb sufficient incident radiation for detection. In addition to the obvious restrictions on the miniaturization of detector arrays and the accompanying signal processing circuitry, this large volume causes radiation hardening problems.

In principle, compound semiconductor materials, which are used for most intrinsic detectors, have all the advantages of the elemental (extrinsic) semiconductors and very few of the disadvantages. $Pb_{1-x}Sn_xTe$ (lead tin telluride) and $PbTe$ (lead telluride; $x=0$) are examples of excellent compound/alloy detectors for long wavelength IR. Lead tin telluride, for example, has several advantageous characteristics. Because of its direct energy gap, lead tin telluride does not require impurity to absorb incident photons, with the result that there are additional 10^4 cm^{-3} available sites for capturing incident signals. Satisfactory operation with relatively thin detector films on the order of $10 \mu\text{m}$ thickness is thus possible. Also, the composition of lead tin telluride can be altered for tuning to the desired portion of the IR spectrum. A composition of approximately $Pb_{0.8}Sn_{0.2}Te$ ($x = 0.2$) is particularly useful because junction-type photovoltaic detectors using films of this composition provide peak response to infrared radiation in the $10-12 \mu\text{m}$ region.

Some growth techniques which have been used successfully for the formation of single crystal IVA-VIA compounds and alloys on other IVA-VIA compounds and alloys have not been successfully applied to insulating substrates. For example, liquid phase epitaxy (LPE) has not been reported in the growth of IVA-VIA compounds on insulators such as the alkali halides and oxide insulators, presumably because of problems in properly nucleating the IVA-VIA material. Yet there are considerable reports of the use of evaporation and sputtering for growing IVA-VIA materials on insulating halide substrates. This area is reviewed by H. M. Manasevit in *J. Crystal Growth*, vol. 22, pg. 125 et seq. (1974). It

should be noted that these processes lead to slow growth rates on insulators, typically less than about 350 \AA/min. ($0.035 \text{ micron/min.}$). This is particularly disadvantageous and impractical for applications where thick films may be required, as in IR detectors. In addition, the composition of the grown film may not be homogeneous, particularly for alloy growth, because the vapor pressures of the source materials are different at a given temperature and must be controlled carefully to produce a film of a desired composition when two or three sources and multi-temperatures are used. Also, the composition of the vapor may differ considerably from that of the source during the evaporation process, since the vapor may consist of elements together with compounds having stoichiometry different from the source, thereby resulting in deposits of non-stoichiometric composition.

As may be thus appreciated, it is highly desirable to have a process which provides (1) a fast rate of growth for IVA-VIA compounds on substrates, (2) multilayer film structures of different compositions and impurity levels and conductivity type without removing the structures from the growth system and (3) large area films of controlled compositions and stoichiometry.

SUMMARY OF THE INVENTION

The instant invention concerns a composite comprising at least one monocrystalline layer or film of IVA-VIA compound or alloy, such as $PbTe$, $Pb_{1-x}Sn_xTe$, PbS , $PbSe$ and $SnTe$, on a monocrystalline inorganic cubic or rhombohedral oxide substrate and a chemical vapor deposition process for forming both monocrystalline and polycrystalline composites. The chemical vapor deposition process utilizes the pyrolysis of a gaseous mixture of IVA-containing metalorganic compounds and VIA-containing metalorganic compounds and/or hydrides on the substrate at a temperature preferably within the range $450^\circ-650^\circ \text{ C.}$ Below about 450° C film growth rates were found to be quite low; above about $550^\circ-650^\circ \text{ C.}$, film deterioration was usually observed on substrates such as NaCl that were not stable at these temperatures. If the film contains lead and the substrate is sapphire or magnesium aluminate (spinel), a layer of lead is preferably formed first on the substrate by pyrolysis of a lead-containing metalorganic compound, followed by pyrolysis of the VIA-containing compounds and then by pyrolysis of appropriate mixtures of IVA- and VIA-containing metalorganic compounds.

By varying the deposition parameters, or by introducing impurities into the gaseous atmosphere, the film conductivity-type is controlled. Composites comprising multilayer films are formed without removing the composite from the deposition system.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partial, cross-sectional view of a IVA-VIA composite embodying principles of the present invention.

FIG. 2 is a partial, cross-sectional view of an alternative composite embodying principles of the present invention comprising multilayer films of IVA-VIA compounds.

FIG. 3 is a schematic diagram of a reactor system for forming IVA-VIA composites, such as those of FIGS. 1 and 2, in accordance with the method of the present invention.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

Referring to FIG. 1, there is shown a cross-sectional view of a composite 10 which may be formed according to the method of the present invention. The composite comprises a monocrystalline layer or film 11 of compounds or alloys of groups IVA and VIA of the Periodic Table, such as PbS, PbTe, PbSe, Pb_{1-x}Sn_xTe and SnTe, epitaxially formed on a monocrystalline substrate 12 such as a semiconductor material or insulative material.

Referring now to FIG. 2, there is shown a cross-sectional view of a multilayer composite 13 which also may be grown according to the method of the present invention. Typically, the composite 13 comprises the substrate 12, an epitaxial monocrystalline layer or film 11 of lead tin telluride or lead telluride, which is of one conductivity type (such as n-type), formed on the substrate 12, and another epitaxial monocrystalline layer or film 14 of lead tin telluride or PbTe of the opposite conductivity type formed on the layer 22. The applications for this multilayer composite 13 include infrared detectors, as described subsequently.

It will be appreciated that where the IVA-VIA film(s) need not be monocrystalline, the substrate 12 may be amorphous, such as glass or fused quartz, or polycrystalline, such as polycrystalline aluminum oxide.

Referring now to FIG. 3, there is shown a schematic representation of a reactor system 20 which may be utilized to epitaxially form IVA-VIA compounds using the method of the present invention. The reactor typically comprises a quartz reactor chamber 21 containing an SiC-covered carbon pedestal 22 for supporting the substrate 12 (FIGS. 1 and 2) and an RF heating coil 23 which is connected to a power source (not shown). Although the dimensions are not critical, a chamber 21 about 6 cm in diameter by 40 cm in length has been used successfully. The temperature of the pedestal 22 and the substrate supported thereon may be measured by an infrared radiation thermometer (not shown) which may control the power to the coil 23. Means (not shown) may be provided for rotating the substrate, as shown by the arrow, to promote uniform deposition.

The reactant gases which form the IVA-VIA compounds enter the reactor chamber 21 via inlet line 24. Line 25 is used to exhaust the chamber of spent and unused reactants and gases, and to connect the chamber to sources of vacuum and air (not shown). The reactor system 20 uses stainless steel bubbler tanks such as tanks 31, 32 and 33 as needed for supplying the IVA-VIA film constituents, and bubbler tanks such as tank 34 for supplying conductivity-type determining impurities (n-type or p-type dopants). Alternatively, the dopants may be introduced in dilute form from a tank 35 containing the dopants and a carrier gas compatible with the growth process, e.g., H₂ or He, if such a dopant mixture is available.

Palladium-purified hydrogen is used as the carrier gas for the film constituents. The carrier gas is flowed from a source 37 through a liquid nitrogen cold trap 38 and through an assembly 39 of valve-controlled flow meters. The purified hydrogen then can be directed at a controlled rate through any or all of valves 41, 42, 43 and 44, respectively, (valves 81, 82, 83 and 84 being closed) into bubbler tanks 31, 32, 33 and/or 34, thereby transporting the desired reactant constituents in the bubblers through tank exit valves 46, 47, 48 and/or 49.

The constituents are then transported through valves 51, 52, 53 and/or 54 and, after proper mixing, through valve 62 to inlet line 24 and the reactor chamber 21. The spent reactant gases are exhausted from chamber 21 via lines 25 and valve 63.

Briefly, the process of forming composites 10 (FIG. 1) having layers or films 11 of IVA-VIA compounds or alloys comprises the steps of 1) evacuating the reactor chamber 21; 2) filling and flushing the reactor chamber with flowing hydrogen; 3) heating the pedestal 22 and pedestal-supported substrate 12 to the deposition temperature; 4) equilibrating the flow of gas from the bubbler tanks by connecting the appropriate tanks to exhaust (via valves 66, 67, 68, 69 and 72) and bubbling hydrogen therethrough at a controlled rate to equilibrate the flows at a predetermined ratio; 5) directing reactant gases into the reactor chamber to form the film of IVA-VIA compound or alloy; and 6) cooling the deposition composite to room temperature in hydrogen after diverting the reactant gases from the reactor. The formation of a layer of lead on the substrates prior to deposition per step 5 is an important part of the process for growing continuous, monocrystalline, lead-containing films 11, such as lead telluride and lead tin telluride, on insulative oxide substrates, such as magnesium aluminate and sapphire.

To evacuate the reactor according to step 1, valve 55 is opened to connect the reactor chamber 21 to vacuum. The flow lines up to the valves of the bubbler tanks 31, 32, 33 and/or 34 may also be connected to vacuum and evacuated through valves 56, 57, 58 and 59, respectively prior to filling with H₂.

According to step 2, the reactor chamber is purged by flowing hydrogen from tank 37 through flow meter valve 61 and inlet valve 78 to the inlet line 24 and the reactor chamber 21, then exhausting the hydrogen from the chamber through line 25 and exhaust valve 63.

The equilibration of gas flow (step 4) may be initiated simultaneously with the equilibration of the temperature of the pedestal 22 (step 3). That is, while the pedestal is being brought to deposition temperature, the hydrogen gas may be flowed through the bubbler tanks, as described previously, and diverted through valves 51, 52, 53 and 54 (valves 66, 67, 68 and 69 and common vacuum valve 70 are closed) to exhaust and equilibrate the flows through valves 75 and 72 at a predetermined ratio. The flows may be controlled using the valves associated with the flow meter assembly 39.

According to step 5, after the pedestal 22 and substrate 12 are at the deposition temperature and the flow rates have been equilibrated, valve 62 is opened, valve 75 is closed and the gas reactants are directed into the reactor chamber 21. It will be noted that the reactant gases are channeled into a single line, inlet line 24, prior to entering the reactor chamber. By channeling the reactant gases into the single inlet line 24, the gases, which are mixed externally to the heated reactor chamber can be introduced simultaneously into the reactor, thereby precluding an undesirable premature reaction of individual reactants with the heated substrate. Also, the valves 66-69 permit individual setting of the gas reactants prior to their mixing and introduction into the reaction chamber. Moreover, the valves 51-54 permit introduction of individual reactants prior to deposition per step 5 to promote the growth of films on materials such as sapphire and magnesium aluminate, as discussed previously.

After a predetermined deposition time involving step 6, the resulting composite is allowed to cool by shutting off power to the RF heating coil 23 after diverting the reactant gases from the reactor chamber 21 and through valves 66-69, 75 (with valve 62 closed), and 72. At the same time, hydrogen is still flowing through the reactor chamber via valves 61, 78, and 63, thereby cooling the sample in flowing carrier gas.

When the reactants and sources of dopant are normally gaseous at room temperature or are sufficiently volatile so that transport by a carrier gas may be considered optional, step 4 of the process can involve equilibrating the flows of these reactants or sources of dopants supplied by tank 35 with the other reactants by connection to the flow system via valve 71. If it is preferred that members of the reactant mixture meet in inlet line 24 of the reactor via separate lines, then the appropriate flows can be directed through valve 77 after adjusting the flows using flowmeter valve 76 and exhaust valve 73, which is closed immediately after valve 71 or 77 is opened. At the end of the deposition, the valve positions are reversed in order to remove (exclude) the reactant gases from the reactor.

FIG. 3 is used for purposes of illustration and instruction as to technique. Modifications in the design are within the capabilities of those skilled in the area of chemical vapor deposition.

SUBSTRATES

The Group II fluorides, particularly BaF_2 , are of considerable interest as substrates for IVA-VIA compounds because their thermal expansions approximate those of the IVA-VIA compounds, and because they are essentially transparent to 10-12 μm radiation in thin wafer form. BaF_2 considered an excellent substrate for IVA-VIA IR detectors at these wavelengths. Also, the insulative metallic oxides sapphire, magnesium oxide (MgO), and magnesium aluminate have properties which make them of interest as substrates for IVA-VIA compounds which can be used as detectors in the 3-5 μm range. For example, except for MgO , they are more stable than fluorides in the atmospheres used for the growth of the films.

BaF_2 and CaF_2 were used primarily in the form of cleaved (111)-oriented wafers made from crystal ingots, although some polished BaF_2 substrates of (111) orientation and (100) orientation which were prepared from (111) oriented crystal ingots were successfully used for monocrystalline film growth. The (111)-oriented BaF_2 and CaF_2 crystal ingots were typically about one inch in diameter and up to one inch in length and were used to form substrates of about 0.020 to 0.030 inch thickness.

In addition to the above, single crystal alkali halides, represented by NaCl , II-VI compounds, represented by CdTe , III-V compounds, represented by GaAs , and IV-VI compounds, represented by PbTe , were used as substrates for the epitaxial growth of the IV-VI compounds. The alkali halides were cleaved just prior to use; the CdTe was a single crystal film grown on a sapphire ($\alpha\text{-Al}_2\text{O}_3$) substrate; and the GaAs were (100) and (111)-oriented single crystal substrates, which were polished by chemical-mechanical means, and as-grown (111)-oriented films on sapphire. PbTe substrates (see Table II, composite type nos. 12 and 13) were polished by chemical-mechanical means and were oriented to expose a (100) plane.

In general it can be expected that the process can be used to produce IVA-VIA films on IVA-VIA substrates which possess similar lattice parameters. See, e.g., the above-mentioned article in *J. Crystal Growth* authored by one of the present inventors which is hereby incorporated by reference. The various metalorganic compounds used for IVA-VIA film growth are listed in Table I below.

TABLE I METALORGANIC COMPOUNDS USED IN DEPOSITION OF IVA-VIA FILMS		
Compound	Abbreviation	Formulation
Tetramethyllead	TM ₄ Pb	(CH_3) ₄ Pb
Tetraethyllead	TE ₄ Pb	(C_2H_5) ₄ Pb
Tetramethyltin	TM ₄ Sn	(CH_3) ₄ Sn
Tetraethyltin	TE ₄ Sn	(C_2H_5) ₄ Sn
Dimethyltellurium	DM ₂ Te	(CH_3) ₂ Te
Diethyltellurium	DE ₂ Te	(C_2H_5) ₂ Te
Trimethylantimony	TM ₃ Sb	(CH_3) ₃ Sb

Hydrogen telluride (H_2Te) is a suitable substitute for DM₂Te as a source of Te.

PbTe FILMS/SAPPHIRE AND MAGNESIUM ALUMINATE (SPINEL) SUBSTRATES

Here, tetraethyllead, TePb , and dimethyltellurium, DM₂Te, were used as the source of Pb and Te, respectively, in the stainless steel bubbler tanks 31 and 33. Polished, (0001)-oriented sapphire and polished, (111)-oriented magnesium aluminate were used as substrates 12 (FIG. 1).

After evacuating the reactor chamber 21 (step 1) and filling the reactor chamber with hydrogen flowing at approximately 10 liters per minute (1 pm), (step 2), the pedestal 22 was heated by the RF coil 23 to within the desired deposition temperature range of approximately 450°-650° C. Hydrogen flow rates of approximately one 1pm through the TEPb and 25-75 cccpm through the DM₂Te were used.

To promote rapid growth of continuous, monocrystalline PbTe films 11 (FIG. 1) on the sapphire and magnesium aluminate substrates 12, the substrate was nucleated with a thin deposit of lead prior to the onset of PbTe deposition. Typically, this was achieved within the preferred deposition temperature range of approximately 450°-650° prior to step 5 (or as an initial substep of step 5) by 1) introducing TEPb alone into the reactor chamber 21 to deposit Pb on the heated substrate, 2) next introducing DM₂Te alone into the reaction chamber, and 3) followed by the reintroduction of TEPb together with the DM₂Te into chamber 21, according to step 5.

More specifically, valves 51 and 62 were opened and valve 66, which had been open to exhaust the TEPb during flow equilibration (step 4), was closed, in order to direct TEPb alone into the reactor chamber 21. As mentioned previously, a hydrogen carrier gas flow rate of one 1pm was used for the TEPb . After about one minute at this flow rate, sufficient Pb growth occurred to form a Pb deposit. Next valve 66 was opened to direct the TEPb to exhaust and valve 51 was closed.

Valve 53 was then opened to introduce DM₂Te into the reactor through valve 62 with valve 68 closed. The DM₂Te converts Pb to PbTe and/or provides a tellurium rich atmosphere. A hydrogen flow rate through the DM₂Te of about 45 cccpm was used. After about five minutes of DM₂Te flow, TEPb was reintroduced into the reactor chamber in the carrier gas in the presence of DM₂Te (step 5) and PbTe was formed in the presence of the Te rich atmosphere.

TABLE II

CRYSTALLOGRAPHIC RELATIONSHIPS,
IVA-VIA FILMS AND SUBSTRATES

COMPOSITE TYPE NO.	SUBSTRATE PLANE	PARALLEL PLANES	PARALLEL DIRECTIONS
1	(0001) α -Al ₂ O ₃	(111) PbTe // (0001) Al ₂ O ₃	[110] PbTe // [1210] Al ₂ O ₃
2	(111) MgAl ₂ O ₄	(111) PbTe // (111) MgAl ₂ O ₄	[211] PbTe // [011] MgAl ₂ O ₄
3	(111) BaF ₂ (cleaved)	(111) PbTe // (111) BaF ₂	[110] PbTe // [011] BaF ₂
4	(100) NaCl	(100) PbTe // (100) NaCl	not determined
5	(100) MgO	(100) PbTe // (100) MgO	not determined
6	(0001) α -Al ₂ O ₃	(111) PbS // (0001) Al ₂ O ₃	[110] PbS // [1210] Al ₂ O ₃
7	(111) BaF ₂ (cleaved)	(111) PbS // (111) BaF ₂	[110] PbS // [011] BaF ₂
8	(111) CaF ₂	(111) PbS // (111) CaF ₂	[110] PbS // [011] CaF ₂
9	(0001) α -Al ₂ O ₃	(111) PbSe // (0001) Al ₂ O ₃	[110] PbSe // [1210] Al ₂ O ₃
10	(111) BaF ₂	(111) PbSe // (111) BaF ₂	[110] PbSe // [011] BaF ₂
11	(111) CaF ₂	(111) PbSe // (111) CaF ₂	[110] PbSe // [011] CaF ₂
12	(100) PbTe	(100) PbTe // (100) PbTe	not determined
13	(100) PbTe	(100) Pb _{0.8} Sn _{0.2} Te // (100) PbTe	not determined

After the film 12 of PbTe was deposited, the gas reactant mixture was diverted from the reactor chamber 21 and the sample was cooled in hydrogen flowing at about one 1pm (step 6).

The PbTe films were grown to about 5 μ m thickness on the sapphire and magnesium aluminate substrates. The films were determined to be monocrystalline using x-ray analysis. The crystallographic relationships between the PbTe films and alumina and spinel substrates are summarized in Table II, under composite type numbers 1 and 2. Growth parameters are summarized in Table III, also under composite type numbers 1 and 2.

PbTE FILMS/BaF₂ SUBSTRATES

PbTe films were grown on single crystal BaF₂ substrates using TEPb or TMPb and DMTe as the reactants. Some substrates were used as-cleaved, without polishing.

Monocrystalline film growth on the cleaved, (111)-oriented BaF₂ substrates was achieved using TEPb as the source of Pb at pedestal temperatures of 450°-600° C. Specifically, temperatures of 450, 500, 560, 575 and 600° C were utilized. Somewhat higher temperatures can also be expected to be consistent with single crystal growth. Also, the range of 500°-600° C provided a growth rate (0.08 μ m/min. or 5 μ m/hr. for the stated parameters) which was approximately twice that achieved at 450° C.

The PbTe films were grown to a thickness of approximately 5 microns. X-ray diffraction measurements showed the PbTe films were monocrystalline. The film-substrate crystallographic relations for PbTe films grown on the cleaved, (111)-oriented BaF₂ are indicated in Table II under composite type no. 3. The growth parameters described above are summarized in Table III under composite type no. 3A.

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TABLE III

GROWTH PARAMETERS FOR IVA-VIA FILMS											
Sample Composite	1	2	3A	3B	3C	3D	3E	3F	3G	3H	
Type No.	(0001) Al ₂ O ₃	(111) Mg-Al ₂ O ₄	(111) BaP ₂						NOT CHARACTERIZED		
Substrate			450- 600	450- 600	450- 600	450- 600	450- 600	450- 600	x80.2 0.2≤x≤0.5	x=0.2	x=0.21 x=0.21
Film									550- 625	550- 625	625
Deposition											
Temp (°C)	500-600										
Carrier Gas Flow Rate (ccpm)											
TMPb	1000	1000	50	100	200	200	1000	1000- 2000	2000	2000	2000
TEPb	—	—	—	—	—	—	—	3000	3000	2000	2000
TESn	—	—	—	—	—	—	—	75- 150	75	75	75
DMTe	25-75	50	75	75	75	35	25	7	20	26	50
TMSb	—	—	—	—	—	—	—	—	—	—	125
Flow Rate (ccpm)											
H ₂ S	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a
H ₂ Se	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a
Growth Rate (μm/hr)											
Film Thickness (μm)	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a
Film Conductivity Type											
Electrical Properties	—	—	—	—	—	—	—	—	—	—	—
Resistivity (ohm-cm)	—	—	—	—	—	—	—	—	—	—	—
Carrier Concentration (cm ⁻³)	—	—	—	—	—	—	—	—	—	—	—
Mobility (cm ² /V-sec.)	—	—	—	—	—	—	—	—	—	—	—
Sample Composite											
Type No.											
Substrate											
Film											
Deposition											
Temp (°C)											
Carrier Gas Flow Rate (ccpm)											
TMPb	1000	1000	100	100	100	100	100	100	100	100	100
TEPb	—	—	—	—	—	—	—	—	—	—	—
TESn	25	25	—	—	—	—	—	—	—	—	—
DMTe	—	—	—	—	—	—	—	—	—	—	—
TMSb	—	—	—	—	—	—	—	—	—	—	—
Flow Rate (ccpm)											
H ₂ S	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a
H ₂ Se	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a
Growth Rate (μm/hr)											
Film Thickness (μm)	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a
Film Conductivity Type											
Electrical Properties	—	—	—	—	—	—	—	—	—	—	—
Resistivity (ohm-cm)	—	—	—	—	—	—	—	—	—	—	—
Carrier Concentration (cm ⁻³)	—	—	—	—	—	—	—	—	—	—	—
Mobility (cm ² /V-sec.)	—	—	—	—	—	—	—	—	—	—	—

^aH₂ flow rates of 50, 2000, 75 ccpm through TMPb, TESn and DMTe, resp.; temp. 625° C.

— indicates data not taken

Similar results were obtained using TMPb as the source of Pb , as shown below, except that growth rates could be increased considerably.

The metalorganic CVD process of the present invention was used successfully to vary the conductivity type. That is, both n- and p-type PbTe films were formed on cleaved (111) BaF_2 substrates. Here, TMPb and DMTe were the sources of lead and tellurium. In these examples, the n-type and p-type films were obtained by varying the TMPb to DMTe ratio. See Table III, composite type no's. 3B-3E. For composite type no. 3D, hydrogen flow rates of 200 cccpm through the TMPb and 75 cccpm through the DMTe gave a TMPb:DMTe flow rate ratio of about 3:1, and provided a high film growth rate of about 32 microns per hour and a very high quality, monocrystalline n-type (presumably metal rich) PbTe film. However, for high TMPb concentrations and low DMTe concentrations, p-type films were formed, perhaps due to a high defect structure. Thus, composite type no. 3E was p-type, when the DMTe flow was lowered from 75 to 35 cccpm. Varying the ratios of TEPb and DMTe can thus be expected to yield n- and p-type films with controllable properties.

N-type on p-type and p-type on n-type multilayer films and junctions were formed by varying the ratios of the Group IVA and VIA reactants.

PbTe FILMS/ NaCl SUBSTRATES

The method and metalorganic constituents used for the formation of PbTe films on BaF_2 substrates were used to form monocrystalline PbTe films on (100)-oriented NaCl substrates. Here, deposition was attempted and achieved at temperatures in the range of 500°-625° C. The crystallographic relationships of the PbTe films and NaCl substrates are listed in Table II under composite type no. 4. Growth parameters are listed in Table III, also under composite type no. 4, for samples grown within the approximate range 500°-550° C. This range produced better quality films on NaCl than higher temperatures. The NaCl substrates appeared to be unstable at higher temperatures.

PbTe FILMS/ MgO SUBSTRATES

The method and metalorganic constituents used for the formation of PbTe/BaF_2 and PbTe/NaCl composites were also used to form monocrystalline PbTe films on MgO substrates. The crystallographic relationships and growth parameters are listed in Table II and III under composite type no. 5. As was true for PbTe/NaCl composites, better quality films were produced within the range 500°-550° C than at higher temperatures.

Similar results can be expected when TMPb is used as a substitute for TEPb .

PbTe FILMS/ GaAs , GaAs -on- Al_2O_3 , and CdTe -on- Al_2O_3 SUBSTRATES

The method and metalorganic constituents used for the formation of PbTe films on BaF_2 and NaCl substrates were used to form epitaxial PbTe films on polished (100) and (111)-oriented GaAs substrates, on (111) GaAs films grown on (0001) Al_2O_3 ; and on (111) CdTe films grown on (1126) Al_2O_3 . Typical flow rates of 50-200 cccpm for TMPb and 75-100 cccpm for DMTe were used at growth temperatures of 500 and 625° C to form films which were very highly doped with respect to the underlying substrate. Because lead telluride (PbTe) is representative of lead tin telluride ($\text{Pb}_{1-x}\text{Sn}_x\text{Te}$), lead tin telluride can be grown on sub-

strates which are suitable for PbTe growth. Thus, using similar conditions and, of course, a source of tin, such as TESn , lead tin telluride can be grown on the above-described substrates.

PbS AND PbSe FILMS

The method of the present invention was also used to form monocrystalline, continuous films of PbS and PbSe on polished (0001) Al_2O_3 , cleaved (111) BaF_2 , and cleaved (111) CaF_2 substrates using a 550° C deposition temperature. The Group VIA source was H_2S and H_2Se . The crystallographic relationships for the $\text{PbS}/(0001)\text{Al}_2\text{O}_3$, $\text{PbS}/(111)\text{BaF}_2$, $\text{PbS}/(111)\text{CaF}_2$, $\text{PbSe}/(0001)\text{Al}_2\text{O}_3$, $\text{PbSe}/(111)\text{BaF}_2$, and $\text{PbSe}/(111)\text{CaF}_2$ film-substrate composites are listed in Table II, under composite type no's. 6-11, respectively. The growth parameters are listed in Table III under composite type no's 6-11.

Referring to Table III, the PbS films for composite types 6-8, and the PbSe films for composite types 9-11 were formed from TMPb and, respectively, H_2S and H_2Se . The H_2S and H_2Se were supplied from tank 35, which is connected to the reactor system through valves 76 and 77 or 76, 71 and 62. Valve 73 or 75 is used to equilibrate the flows from tank 35 prior to introduction into line 24 and reactor 21. Valve 75 is also used in mixing the H_2S or H_2Se (a carrier gas is optional) from tank 35 with the carrier gas-transported reactants from the bubbler tanks prior to entry into the reactor chamber 21 (step 5).

When the substrate is stable to the Group VIA reactants at the growth temperature and the product of decomposition does not form a deposit on or react with the substrate surface, the Group VIA reactant can be introduced into the reactor prior to the introduction of the Group IVA reactants. For example, reaction of BaF_2 with DMTe precluded introducing DMTe into the reactor prior to the introduction of TEPb or TMPb and mixing of the reactant gases external to the reactor was, therefore, required. In the case of the Group VIA hydrides, namely H_2S and H_2Se , which did not appear to react with BaF_2 , it was sufficient to introduce the VIA containing reactants either singly or together into the reactor prior to the introduction of the metallorganic Pb and/or Sn compounds. Referring to FIG. 3, in the latter case, the Group VIA component would pass through valve 77 into reactor 21 prior to the admittance of the Group IVA component(s) through valve 62.

It will be appreciated by those skilled in the art that pyrolysis of mixtures of the hydrides of S and Se with the Group IVA components will form Group IVA- $\text{S}_{1-x}\text{Se}_x$ compounds such as $\text{PbS}_{1-x}\text{Se}_x$ or $\text{SnS}_{1-x}\text{Se}_x$.

$\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ FILMS/ BaF_2 SUBSTRATES

Lead tin telluride films were grown on cleaved, (111)-oriented BaF_2 substrates at deposition temperatures of 550°-625° C using essentially the lead telluride-on-barium fluoride deposition method with the added film constituent—tin—being supplied by TESn from stainless steel bubbler tank 32. Film growth of composition $x = 0$ to $x = 0.2$ was achieved for hydrogen flow rates through the TESn of up to 2000 cccpm. (As the hydrogen flow rate through the TESn is decreased to zero, the film composition approaches that of lead telluride). Using a hydrogen flow rate of 25 cccpm through the DMT and 1000 cccpm through the TEPb , the desired composition for detector devices, $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ or $x = 0.2$, was closely approximated over a wide range of

hydrogen flow rates (approximately 750-2000 cccpm) through the TESn. Precisely the desired composition was achieved for hydrogen flow rates through the TESn of 850 and 900 cccpm. Growth rates using the temperature range 550°-625° C and the range of hydrogen flow rates of 750-2000 cccpm were approximately 7 to 8 microns per hour. See Table III, composite type No. 3F.

Lead tin telluride films were also grown using TMSn in place of TESn. However, the TMSn was considerably less efficient than TESn for the deposition temperature used, 550°-600° C.

Referring to Table III, composite type No. 3G, growth rates of about 7-23 $\mu\text{m}/\text{hr}$. were obtained over the temperature range 550°-625° C using TMPb in place of TEPb, for a DMTe flow rate of 75-150 cccpm, a TESn flow rate of 3000 cccpm, and a TMPB flow rate of approximately 50 cccpm. Growth rates increased with temperatures in the range 550°-625° C. However, at the higher temperatures, the value of x increased. To control the film composition to $x = 0.2$ at 625° C it was necessary to use a TESn flow rate of about 2000 cccpm, indicated below.

For hydrogen flow rates through the respective reactants TMPb, TESn and DMTe of 50, 2000 and 75 cccpm and a pedestal temperature of 625° C, a film of composition $\text{Pb}_{0.80}\text{Sn}_{0.20}\text{Te}$ was grown to a thickness of approximately 15 micron at a growth rate of about 23 micron per hour on (111) BaF_2 substrates. The film possessed excellent electrical properties at room temperatures: resistivity was approximately 0.0014 ohm-cm; hole concentration was $9.5 \times 10^{18} \text{ cm}^{-3}$; mobility was about 470 $\text{cm}^2/\text{V}\cdot\text{sec}$; and the band-gap energy was about 0.23 eV.

Sawed and polished (111) BaF_2 wafers were also used as substrates. The appearance of lead tin telluride films grown on polished BaF_2 substrates was inferior to those grown on freshly cleaved BaF_2 , but the electrical properties were essentially the same.

Using the foregoing information, those skilled in the art will achieve film compositions within the range $0 \leq x \leq 0.5$.

VARIED CONDUCTIVITY-TYPE $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ FILMS

The conductivity type of lead tin telluride films was changed by varying the DMTe flow rate and growth temperature. As shown by the data in Table III, alkyl antimony compounds such as TMSb can also be used as a source of n-type doping impurity to vary the conductivity type of lead tin telluride. Referring to FIG. 3, 50 TMSb was stored at -78° C in the stainless steel bubbler tank 34. Hydrogen was used to transport the TMSb for mixing with the other reactants externally to the reactor chamber 21.

As shown by composite nos. 3H-3L in Table III, 55 increasing the TMSb flow rate changes the film from p-type to n-type. The TMSb flow rate at which this type change occurs is dependent upon the other parameters, such as TMPb, TESn and DMTe flow rates and film growth temperature. Table III indicates the film composition can be closely controlled and that electrical properties for the p-type and n-type films are generally excellent.

Considerable tensile stress was present in PbTe and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ films grown on BaF_2 substrates, mainly 65 because of the large difference between the thermal expansion coefficients of the film materials and the BaF_2 substrate material. To illustrate, BaF_2 and PbTe

have coefficients of approximately $18 \times 10^{-6}/^\circ\text{C}$ and $27 \times 10^{-6}/^\circ\text{C}$, respectively. However, despite the existence of stress, $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ films 100 microns thick were grown on BaF_2 substrates without evidence of cracking. Such composites may be useful as strain gauges, etc.

DOUBLE LAYER $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ FILMS/ BaF_2 SUBSTRATES

Referring now to FIG. 2 using a cleaved, (111)-oriented BaF_2 substrate 12, a first, undoped p-type layer 11 of $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ was epitaxially formed on the substrate, then a second $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ layer 14 doped with Sb was grown on the first layer. Both layers were formed using the method of the present invention, as described previously. The double layer, $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$ film- BaF_2 substrate composite 13 was processed into a mesa diode (not shown) by standard photolithographic techniques. Ohmic contact was provided by vacuum deposition of a one micron thick film of Sn on the surface of the upper layer 14. An infrared photovoltaic effect of about 25 mV was observed at 77° K.

Sn-VIA FILMS

The reaction of TESn with DMTe, H_2S and H_2Se was used to form Sn-VIA compound films. For each film, the new H_2 flow through the TESn was kept constant at 2000 cccpm. The flow through DMTe and the H_2S and H_2Se flows were arbitrarily set at 75 cccpm, ~25 cccpm, and ~50 cccpm, respectively.

Within the temperature range ~500°-650° C, ordered growth of SnTe was obtained on the substrates examined, cleaved (111) BaF_2 and polished (100) PbTe . Considerable trigonal structure usually associated with (111) growth was obtained on the BaF_2 , particularly near the edges of the substrate. Growth on (100) PbTe produced a large array of islands oriented with respect to each other and the substrate. Large crystallites with parallel faces and, in some cases prominent hollow centers grew at the edges of the PbTe substrates under these less-than-optimum growth conditions.

S and Se chalcogenides of tin were grown over the deposition temperature range of ~500°-575° C. Above 575° C, e.g. at 600° C, film quality decreased. The VIA constituents S and Se were provided by H_2S and H_2Se , respectively, using arbitrarily-chosen flow rates of ~25 and ~50 cccpm, respectively.

The nature of the growth of the S and Se chalcogenides of Sn, which possess an orthorhombic structure, was not like that of cubic SnTe. Tinsulfide films, ~3 μm thick, grown at 550° C simultaneously on cleaved BaF_2 and CaF_2 tended to peel from the BaF_2 but adhered to the CaF_2 . At 500° C tin selenide grew as crystallites on BaF_2 . An orienting influence of the substrate was suggested by the parallelism and 60 degree symmetry displayed by many of the crystallites. In the early growth stages the films possessed a yellow-orange color; thicker films were grey. Crystallite growth of both compounds was obtained on (0001) Al_2O_3 .

Continuous film growth of the tin-VIA compounds on sapphire can be expected if the surface is nucleated with Sn prior to the growth of the tin-VIA compounds, as previously described for PbTe growth on sapphire and magnesium aluminate.

Thus, there has been described a method of growing VIA-VIA films on insulative and semiconducting substrates. Examples of the method of growth, of the film-substrate composites formed thereby, and of applica-

tions for the composites have been described. However, the scope of the invention is limited only by the appended claims.

Having thus described a preferred embodiment, what is claimed is:

1. A method for forming a layer of Group IVA-VIA material on an amorphous substrate of glass or fused quartz or a monocrystalline or a polycrystalline substrate selected from the group consisting of Group IA - Group VIA compounds, Group II - Group VI compounds Group IIA - Fluorides, Group IIIA - Group VA compounds and Group IV - Group VI compounds, α - Al_2O_3 and MgAl_2O_4 , comprising the steps of:

establishing a heated deposition zone at a temperature within the range 400° - 700° C and encompassing a deposition surface of said substrate; forming a gaseous mixture of metalorganic IVA-containing and VIA-containing components; and pyrolyzing said mixture within said heated deposition zone.

2. A method for forming a layer of Group IVA-VIA material on a substrate as defined in claim 1 wherein: the layer of IVA-VIA material is a monocrystalline layer of PbS or PbSe ;

the Group VIA containing component is selected from H_2S or H_2Se ; and

the Group VIA-containing component is introduced into the heated deposition zone prior to introduction of the Group IVA-containing component.

3. A method for forming a layer of Group IVA-VIA material on a substrate as defined in claim 1, wherein the substrate is a monocrystalline Group IA-VIIA material.

4. A method for forming a layer of Group IVA-VIA material on a substrate as defined in claim 1, wherein the substrate is a monocrystalline Group IIA-fluoride material.

5. A method for forming a layer of Group IVA-VIA semiconductor on a substrate as defined in claim 1, wherein the substrate and layer are monocrystalline, the group IVA-VIA material is selected from lead telluride and lead tin telluride, and the substrate is selected from α - Al_2O_3 and magnesium aluminate, the method further comprising the step of forming a layer of Pb on the deposition surface of the substrate prior to the formation of lead telluride or lead tin telluride.

6. The method for forming a layer of Group IVA-VIA semiconductor material on a substrate as defined in claim 1, wherein the Group IVA-VIA material is a tin-VIA material and the substrate is selected from α - Al_2O_3 and magnesium aluminate the method further comprising the step of forming a layer of tin on the deposition surface of the substrate prior to the formation of the tin-VIA material.

7. The method defined in claim 6 wherein the VIA constituent of the tin-VIA material is at least one element selected from the group consisting of sulfide, selenide and telluride.

8. A method for epitaxially forming at least one monocrystalline layer of IVA-VIA semiconductor material on a deposition surface of a monocrystalline substrate selected from the group consisting of Group IA - Group VIA compounds, Group II - Group VI compounds, Group IIA - Fluorides, Group IIIA - Group VA compounds and Group IV - Group VI compounds, α - Al_2O_3 and MgAl_2O_4 , said IVA constituent being selected from Pb and Sn and said via constituent being selected from S , Se and Te , the method comprising the step of:

establishing a heated, deposition zone at a temperature within the range 450° - 650° C and encompassing the deposition surface of the substrate;

forming a gaseous mixture of IVA-containing compounds selected from the group consisting of tetraethyllead, tetramethyllead, tetramethyltin, tetraethyltin, and of VIA-containing compounds selected from the group consisting of dimethyltellurium, H_2Te , diethyltellurium, hydrogen sulfide, and hydrogen selenide; and

pyrolyzing said gaseous mixture within said deposition zone.

9. A method for epitaxially forming at least one monocrystalline layer of IVA-VIA semiconductor material on a deposition surface of a monocrystalline substrate as defined in claim 8, wherein the VIA-containing compound is hydrogen sulfide or hydrogen selenide and is introduced into the deposition zone prior to the introduction of the IVA-containing compound.

10. The method defined in claim 8, further comprising the steps of:

varying the ratio of said IVA-containing and VIA-containing compounds in said mixture to form layers of different compositions; and selectively introducing conductivity-type determining impurities into said gaseous mixture.

11. The method defined in claim 10 wherein the conductivity-type determining impurity is Sb and is supplied by a metalorganic alkyl compound of Sb .

12. The method defined in claim 10 wherein the monocrystalline substrate is selected from the group consisting of Group IA-VIIA, Group IIA-fluoride, Group IIIA-VA, and Group IIB-VIA materials.

13. The method recited in claim 1 wherein said substrate is monocrystalline.

14. The method recited in claim 1 wherein said substrate is polycrystalline.

15. The method recited in claim 1 wherein said substrate is amorphous.